



**Innovative Technology Development for Comprehensive Air
Quality Characterization from Open Burning**
SERDP WP-2153
Final Report



U.S. Army Engineer Research and Development Center
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14. ABSTRACT Work on WP-2153 included a field campaign to characterize air emissions from open burning (OB) in pans of three propellants (M31A1E1, M26 and SPCF) and static firing of Sparrow rocket motors (containing ammonium perchlorate (AP) composite propellant). An aerostat-lofted instrument package called the "Flyer" was used as the sampling platform. Continuous measurements of CO ₂ and CO, and batch samples for particulate matter (PM ₁₀ and PM _{2.5}), metals, HCl, perchlorate, chlorate, volatile organic compounds, and semi-volatile organic compounds allowed determination of emission factors. CO ₂ readings indicated that the Flyer was successfully maneuvered into 90-98% of the OB plumes from pan burning of the three different propellant types and 92% of the static firing plumes. The calculated emission factors in general were comparable to earlier results and literature values for similar propellant types. The resulting emission factors for PM ₁₀ and PM _{2.5} were very close suggesting that OB plumes generate mostly fine PM (PM _{2.5}). No perchlorate and CO were detected for any of the propellants. Only a very limited number of static fire events were sampled and additional work is necessary to close material balances for Cl and Al in the AP propellant.					
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Abstract

For many decades, Open Burning/Open Detonation (OB/OD) has been used as a safe, effective, and economic way to demilitarize munitions for energetic material disposal. Field OB/OD air emissions have been very difficult to characterize because of rapid dispersion, short event duration, heterogeneous emission concentrations, large plume lift, soil entrainment, and explosive safety restrictions. Work on SERDP project WP-2153 is a continuation of work on SERDP project WP-1672 “Feasibility of New Technology to Comprehensively Characterize Air Emissions from Full Scale Open Burning and Open Detonation” which was successfully completed in FY10. Work on SERDP WP-1672 determined that an aerostat-lofted instrument sampling package called the “Flyer” seemed to be a feasible measurement platform for determining emission factors for the OB of propellants and the OD of explosives.

In order to meet the objectives of SERDP WP-2153, we conducted a field campaign to characterize air emissions from OB in pans of three propellants (M31A1E1, M26 and SPCF) and static firing of Sparrow rocket motors (containing ammonium perchlorate (AP) composite propellant). The field campaign occurred over a three week period from March 19 through April 7, 2011 at Tooele Army Depot, UT. The research team also studied the feasibility of using the Flyer to characterize air emissions from soil-covered OD.

During the field campaign, the Flyer was maneuvered into the OB and static fire plumes for sampling. The 46 lb (21 kg) instrument package was lofted with a He-filled balloon of 16 ft (4.9 m) nominal diameter, maneuvered by two tethers connected to two vehicles. Continuous measurements of CO₂ and CO, and batch samples for particulate matter (PM₁₀ and PM_{2.5}), metals, HCl, perchlorate, chlorate, volatile organic compounds, and semi-volatile organic compounds allowed determination of emission factors. CO₂ readings indicated that the Flyer was successfully maneuvered into 90-98% of the OB plumes from pan burning of the three different propellant types and 92% of the static firing plumes.

The resulting emission factors for PM₁₀ and PM_{2.5} were very close suggesting that OB plumes generate mostly fine PM (PM_{2.5}). The calculated emission factors were compared to the first year results and literature values for similar propellant types. The derived emission factors for Pb and Ba from SPCF and M26, respectively, were in the same range as the Pb emission factor from the first year study of M1 propellant during WP-1672. HCl was measured from the Sparrow rocket motor OB plumes with two different sampling methods, each resulting in comparable emission factors. The derived HCl emission factor was approximately ten times lower than found in the literature. Chlorate was also detected but was very close to the method reporting limit. No perchlorate and CO were detected for any of the propellants. Low levels of these emissions are expected with complete combustion of propellants.

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List of Acronyms

<u>Term</u>	<u>Definition</u>
AMCCOM	US Army Armament, Munitions and Chemical Command
AP	ammonium perchlorate
AP42	USEPA Compilation of Air Pollutant Emission Factors
ATV	all terrain vehicle
BC	background corrected
BLDC	brushless direct current
CAS	Columbia Analytical Services
CEM	continuous emissions monitor
CFR	Code of Federal Regulations
CV	coefficient of variance
DAC	U.S. Army Defense Ammunition Center
DoD	Department of Defense
EF	emission factor
EFF	environmental fate factor for target analyte i (lb/lb i in ordnance)
ERDC-CERL	Engineer Research Development Center, Construction Engineering Research Laboratory
GC/FID	gas chromatograph(y) - flame ionization detector
GC/MS	gas chromatography/mass spectrometry
GPS	global positioning system
ISO	International Organization for Standardization
JOCG	Joint Ordnance Commanders Group
LIDAR	light detection and ranging
L/min	liters per minute
MCE	mixed cellulose ester
MRL	method reporting limit
MPL	micropulse light detection and ranging (LIDAR)
NA	Not analyzed
NEW	net explosive weight
NDIR	nondispersive infrared
NIOSH	National Institute of Safety and Health
NRMRL	USEPA National Risk Management Research Laboratory
NS	not sampled
OB	open burning
OD	open detonation
OP-FTIR	open-path Fourier transform infrared spectrometer
ORS	optical remote sensing
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
PM _{2.5}	particulate matter that is 2.5 micrometers or smaller in aerodynamic diameter
PM ₁₀	particulate matter that is 10 micrometers or smaller in aerodynamic diameter
ppm	parts per million
PUF	polyurethane foam

<u>Term</u>	<u>Definition</u>
QAPP	quality assurance project plan
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
SERDP	Strategic Environmental Research and Development Program
SPCF	smokeless powder (SP) stabilized by ethyl centralite (C) that also contains a non-combustible flash inhibitor (F)
SVOC	semi-volatile organic compound
TEOM	tapered elemental oscillating microbalance
TNT	2,4,6-trinitrotoluene
USEPA	United States Environmental Protection Agency
UV-DOAS	ultraviolet differential absorption spectrometers
VOC	volatile organic compound

1. Introduction

1.1 Project Overview

U.S. Department of Defense (DoD) Installations, especially demilitarization facilities and Army Ammunition Plants, have long used Open Burning/Open Detonation (OB/OD) as a safe, effective, and economic means to dispose of propellants, explosives, and waste military munitions. DoD installations are required to comply with the Resource Conservation and Recovery Act (RCRA) to operate OB/OD facilities. RCRA permits provide annual limits on the amount of energetic materials that can be disposed of at OB/OD facilities. The permit limitations are based on human health risk assessments that include evaluation of risks from airborne exposure to emissions generated from OB/OD. These assessments have used emission factors developed from open atmosphere testing as well as from a small-scale OB/OD chamber known as a *BangBox*®. Improvements to the methods and equipment for conducting open atmosphere air emissions testing for OB/OD can help to continually validate these emission factors as well as produce a larger set of high quality emission factors that address known data gaps. Field OB/OD air emissions have been very difficult to characterize because of rapid dispersion, short event duration, heterogeneous emission concentrations, large plume lift, soil entrainment, and explosive safety restrictions.

Work on SERDP project WP-2153 is a continuation of work on SERDP project WP-1672 “Feasibility of New Technology to Comprehensively Characterize Air Emissions from Full Scale Open Burning and Open Detonation.” which was successfully completed in FY10. The project team conducted a field campaign at Tooele Army Depot, Utah, in March 2010. Emissions from OB of M1 propellant and uncovered OD of TNT were sampled over a three week period using a combination of air emission measurement systems. Close coordination with the DoD demilitarization community enabled the research team to show the feasibility of some of the sampling systems and to produce useful data for demilitarization-related compliance issues and operations. Work on WP-2153 included OB emissions characterization of several propellants using a subset of the measurement systems employed in WP-1672.

1.2 Objectives

The objectives of WP-2153 were to:

1. Provide innovative field scale measurement methods capable of obtaining representative air emission data and filling OB air emission factor data gaps.
2. Conduct a field campaign to measure emissions of CO₂, CO, PM₁₀ and PM_{2.5}, metals (e.g., Pb and Al), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), HCl, ClO₃⁻, ClO₄⁻, and other chlorinated compounds.

3. Compile OB and static fire field emission factor data and develop capability to measure emissions from field scale OB using single-, double-, triple-based propellants and the static-firing of rocket motors containing aluminized ammonium perchlorate (AP) propellant.

1.3 Background

1.3.1 Previous OB/OD Emission Work

Between 1961 and 1981, Ornellas conducted a series of bomb calorimeter detonation experiments designed to determine how various factors affected the efficiency and effectiveness of the detonation process (Ornellas, 1982). His experiments established that the major reaction products from an unconfined detonation were N_2 , CO_2 , and H_2O , and the minor products were CO , H_2 , CH_4 , NO , NO_2 , HCN , HCl , HF , and volatile organic compounds (VOCs). The first comprehensive DoD study to characterize air emissions from real world OB/OD operations was conducted at Dugway Proving Grounds from 1984 through 1986. In 1988, the U.S. Army conducted a follow-on study in the bang box at Sandia National Laboratories. Based on these test results, DoD concluded that the emission factors for the predominant emission products produced in the bang box emission tests were statistically equivalent to those produced in the Dugway Proving Grounds open range tests. Similarities were also observed in data produced by Ornellas, which showed that emission products did not change substantially, even when the quantity detonated increased 32,000 times. In 1992, the USEPA concurred with these DoD conclusions and agreed to accept bang box produced emission factors as representative of those that would be derived through ground level, open air detonation and burn tests. Work by (Lindsay et al. 1999) employed blimp sampling at Hill Air Force Base in 1998 and 1999 to characterize emissions from OD. The emissions were sampled via canisters, silica tubes, and Teflon filters suspended from the blimp for CO_2 , VOCs, chloride analyses, and particulate matter. The tests were partially successful, showed the potential for this type of sampling platform, and the authors made significant suggestions for improvements.

DoD has submitted draft AP-42 air emission data for OB/OD to USEPA (AP-42 2009). The submission package was put together under a Joint Ordnance Commander's Group Demilitarization and Disposal Subgroup and DAC initiative and is in the final stages of review at the USEPA. However, USEPA is currently working on revising their procedures for submission and publication of all air emission factors, so JOCG Demilitarization and Disposal Subgroup and JOCG Environmental Subgroup are working with USEPA to evaluate how past data, as well as current and future data such as that from this project, will be incorporated into these new procedures and system. The supporting studies included testing on an open test range and in a BangBox® at Dugway Proving Grounds between 1989 and 1995 (U.S. Army, AMMCOM, 1992(a-f); Mitchell et. al., August 1998). The *Naval Air Weapons Station China Lake* also has an ongoing program for OB/OD air emissions research.

The draft Chapter 16 of AP-42 contains tables showing emission factors and emission factor quality ratings for both OB and OD operations. The USEPA quality rating codes for the emission

factors range from A (excellent) to D (below average). A large majority of emission factors are rated C or better. Emission factors with a D rating include PM₁₀ from OD and metals from OD. The proposed draft Chapter 16 has no emission factors for PM_{2.5} or any emission factor data for soil-covered OD.

1.3.2 Summary of WP-1672

WP-1672 consisted of in- situ and optical remote sensing (ORS) sampling, analysis, and monitoring (Kim et al., 2010). The final technical report is available at the SERDP/ESTCP web site (<http://www.serdp.org/content/download/9560/122378/file/WP-1672-FR.pdf>). The in situ sampling configuration included fixed position samplers and airborne sampling. The aerial platform used a balloon-lofted instrument package called the “Flyer.” The instrument pack was lofted with a He-filled balloon and maneuvered by two tethers connected to two all-terrain-vehicles (ATVs). Continuous measurements of CO₂ and co-sampled PM₁₀, volatile organic compounds, and semi-volatile organic compounds allowed the determination of emission factors through a carbon mass balance method.

The ORS monitoring consisted of a system for gases and a system for PM that included: 1) active and passive open-path Fourier Transform Infrared (OP-FTIR) spectrometers and Ultraviolet Differential Absorption Spectrometers (UV-DOAS), and 2) a hybrid-ORS that includes Micropulse Light Detection And Ranging (LIDAR) (MPL) and in situ point measurements. The hybrid-ORS system was complemented with two Tapered Elemental Oscillating Microbalances (TEOMs) and anemometers. The first ORS system measured gaseous emissions with active and passive OP-FTIR and UV-DOAS. The hybrid-ORS system measured light extinction values with the MPL and real time PM₁₀ concentrations with the TEOMs. The MPL was mounted on a positioner to scan “slices” of the plume in vertical directions. The TEOMs were placed on a scissors lift and raised about 30 feet off the ground. Wind speed and wind direction, the duration of each event, and the mass of energetic that was detonated or burned for each event were then used to determine gas and PM₁₀ mass emission factors for OB and OD sources.

Both in situ and ORS measurements have strengths and weaknesses in terms of their abilities to effectively sample or detect emissions in OB/OD plumes. The methods evaluated in WP-1672 were designed to complement each other. During the field campaign, we experienced a wide range of weather conditions typical of Tooele Army Depot in March including rapid and drastic changes in wind direction and speed, strong solar radiation, and precipitation. The changing and unpredictable wind conditions were challenging and each measurement system was most effective under different conditions:

- Aerial sampling by the tethered balloon was very effective during both low and high wind speeds. The mobility provided by the ATV arrangement and the use of highly trained aviation experts enhanced the sampling effectiveness.

- The MPL was effective under most conditions due to its ability to scan through complete vertical slices of the passing OB and OD plumes. Higher wind speeds limited the number of complete scans the MPL could make through the plume.
- Ground-based ORS and TEOM plume detection and sampling effectiveness was enhanced at high wind speeds which held the plume close to the surface and greatly reduced at low wind speeds where thermal diffusion resulted in rapidly rising plumes with limited horizontal transport.

For the OD of TNT, the PM₁₀ emission factor derived from Flyer measurements was 0.13 lb/lb net explosive weight (NEW), the emission factor derived from the ORS-based PM measurement method was 0.20 lb/lb NEW, and the published emission factor is 7.2 lb/lb NEW (AP-42 2009). Although the ORS-based PM measurement method emission factor was almost twice that of the Flyer derived value, the two values were still remarkably close considering the fundamental difference in the two measurement systems. The published value is much higher indicating the potential importance of local conditions on the amount of soil PM that can be entrained in an OD plume.

For the OB of M1 propellant, the PM₁₀ emission factor derived from Flyer measurements was 5.7E-03 lb/lb NEW, the emission factor derived from the ORS-based PM measurement method was 6.5E-03 lb/lb NEW, and the published emission factor was 6.9E-03 lb/lb NEW (AP-42 2009). This close agreement is strong evidence that both PM measurement systems used in the field campaign worked well for OB PM₁₀ emissions. Although both PM measurement systems had success during the Tooele field campaign, the Flyer-based system was in general more flexible during all wind conditions and was chosen as the measurement system to characterize OB PM emissions for WP-2153.

The emission factors for the two target gases (i.e., benzene and naphthalene) derived from Flyer measurements of OB and OD were quite close to existing published values (AP-42 2009). The Flyer was also able to measure other polycyclic aromatic hydrocarbons and these emission factors were again comparable to published values when they were available (AP-42 2009). These results and the proven capability of using the balloon to place the Flyer in the plume are strong indicators of the Flyer measurement system's capability to accurately assess both volatile and semi-volatile organic gas emissions.

In contrast, the ORS measurement systems were not able to detect the target gases and therefore no comparison could be made between the two types of gas measurement systems. The OP-FTIR was able to consistently detect CO and sporadically detect NO, NO₂ ethylene, ammonia, and acetylene. The OP-FTIR was able to measure CO₂ for most OB events but the correlation between CO and CO₂ was very poor. For OD, very few of the plumes where CO was detected also had a corresponding CO₂ detection. The emission factors derived from OP-FTIR measurements for CO were 8.1E-03 lb CO/lb NEW for OB and 6.0E-02 lb CO/lb NEW for OD. This corresponds to 2.2 E-02 lb CO/lb C for OB and 1.6E-01 lb CO/lb C for OD and the published values for CO emission factors are 8.2E-04 lb CO/lb C for OB and 1.5E-01 lb CO/lb C for OD (AP-42

2009). The OD CO emission factor derived from the OP-FTIR measurements is very close to the published value while the OB CO emission factor is not. The UV DOAS detected NO in OB and OD plumes but provided no additional information when compared to the OP-FTIR data. The two passive FTIRs did provide results for some plumes but the results were often contradictory and the information provided no additional benefits beyond what we achieved with OP-FTIR. In general, the ORS monitoring for gasses produced poor or inconsistent results and the research team decided not to continue this type of monitoring for this proposed effort.

2. Materials and Methods

Prior to the field campaign at Tooele Army Depot, the USEPA sampling group developed a Quality Assurance Project Plan (QAPP) that described the propellants to be tested, the test range, testing procedures, sampling methods, analytical methods, and emission factor development. The QAPP for WP-2153 is an addendum to the QAPP developed for WP-1672 and another addendum to the QAPP covers sampling and analysis methods for Cl species. The original QAPP is attached in Appendix A, the WP-2153 addendum that was approved by our advisory group before the field campaign in Appendix B, and the Cl species QAPP in Appendix C.

2.1 Ordnance and Test Range

The air emissions from the OB of a single-base, a double-base and a triple-base propellant were characterized. The air emissions from the static firing of rocket motors containing an aluminized AP propellant were also characterized. These emissions characterization studies were done at the Tooele Ammunition Depot Test Range. These propellants and their composition are listed in Table 2-1. As a comparison the table includes composition data from the M1 propellant tested during WP-1672.

Table 2-1. Notable features of selected propellants.

Compound	Triple base M31A1E1 %	Double base M26 %	Single base SPCF %	AP base Sparrow Rocket Motor %	Single base M1 (2010) %
Potassium (K)	0.56	0.27	0.45		
Chlorine (Cl)				23	
Lead (Pb)			0.78		0.78
Aluminum (Al)				7.5	
Barium (Ba)		0.39			
Molybdenum (Mo)				0.29	
Iron (Fe)				0.44	
Carbon (C)	18	25	26	11	29

SPCF – smokeless powder (SP) stabilized by ethyl centralite (C) that also contains a non-combustible flash inhibitor (F), AP – Ammonium perchlorate propellant with 0.64% w/w Fe_2O_3

These propellants were selected by the U.S. Army Defense Ammunition Center (DAC) with criteria of stockpile relevance, sampling method gaps, and emission factor data gaps. As shown in Table 2-1, notable features of the selected propellants are that the AP propellant contained 23% Cl and 7.5% Al, the SPCF and M1 contained 0.8% Pb, and the M26 contained 0.4% Ba.

The propellants were placed in reusable metal pans situated on a concrete pad (~65 ft × 80 ft, ~20 m × 25 m) then ignited (Figure 2-1). Each pan held a single propellant charge size of 212-397, 333, and 220 lb [96-180, 151, 100 kg] for M31A1E1 (triple base), M26 (double base), and SPCF (single base) propellants, respectively. The charge size for the M1 propellant in 2010 was 100 lb [45 kg]. Additionally, the Sparrow rockets contained 134 lbs [61 kg] NEW and 103 lbs

[47 kg] of AP (Figure 2-1D). Four rockets were lowered into an individual, below ground silo located at the Tooele Production Range then ignited sequentially, about 15 s apart.

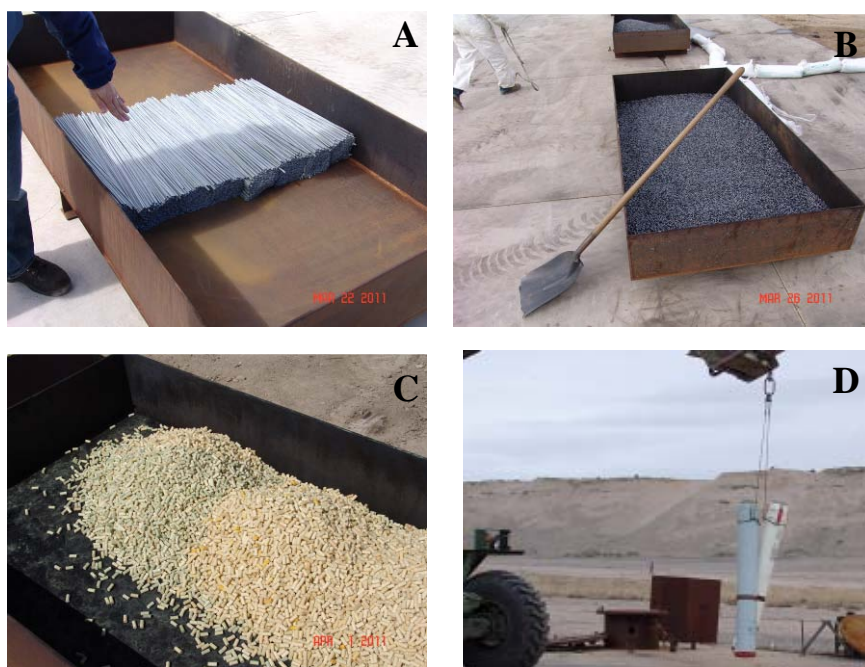


Figure 2-1. Reusable burn pans showing A) M31A1E1, B) M26, C) SPCF, and D) Sparrow rocket motor.

2.2 Aerostat Sampling Method

An aerostat-borne instrument package named the “Flyer” was used to sample emissions from OB in pans and static firing of rocket motors. This aerial sampling method used one ground-based all-terrain vehicle (ATV) and one 4×4 wheel truck, each with an electric winch for the 1000 ft [305 m] tethers, to anchor and maneuver a helium-filled aerostat, which carried a Flyer (Figure 2-2). A Kingfisher (K16N) 16×13 foot-diameter [4.9×3.9 m-diameter] helium aerostat lofted the 46 lb [21 kg] Flyer in Tooele. The combination of two vehicles and two tethers permitted the positioning of the aerostat, and therefore the Flyer, at a specific location and height downwind of the burn pans and static fire silos. After the initiation of the burns, the Flyer was repositioned by controlling the electric tether winches.



Figure 2-2. Aerostat with Flyer.

A number of advances were made to the Flyer, for WP-2153 (Figure 2-3). Two Flyers were built; “Wilbur” and “Orville.” Both were constructed with a lightweight, aluminum frame structure. Wilbur includes an on-board computer, control software, and a wireless transmitter which allows the sampling to be controlled from the ground while incorporating “triggers” that control multiple on/off switches. These triggers, for example, allow one to loft multiple summa canisters and trigger their valve opening at different CO₂ concentrations. The added computer enables data storage like the original Flyer used for WP-1672 and enables the ground crew to monitor CO₂ concentration, battery life, and pressure drop across a filter. Monitoring these data remotely allows maximization of flight time and optimization of sample collection by avoiding problems such as premature battery change outs or battery depletion and signaling the need for changing plugged filters. Orville contains WP-1672 Flyer technology but has been outfitted with a telemetry system to transmit data to a handheld station. The telemetry system enables the ground crew to monitor CO₂ concentration, battery life, and pressure drop across a filter but not control the trigger settings from the ground. Both Flyers were updated with a stronger blower for sampling of semi-volatile compounds, and 48 V Li-ion batteries. The combination of the more complex Wilbur and the upgraded Orville allow us control and monitor from the ground level control center while providing system redundancy in case of failures.

The Flyer was configured for this project with a CO₂ continuous emissions monitor (CEM), CO electrochemical cell, volatile organic compound (VOC) sampler using a Summa canister, semi-volatile sampler using a polyurethane foam (PUF)/XAD-2 resin/PUF sorbent, PM₁₀ and PM_{2.5} filter sampler, HCl sampler using a filter and silica sorbent, perchlorate filter sampler, and a PM_{2.5} CEM sampler. The specific samplers used for each propellant were selected based on the anticipated emission products. Table 2-2 shows the specific emissions analyzed for each propellant. In addition, the Flyer also has a global positioning system (GPS) on board to pinpoint position and altitude. All sensor data and flow rates were logged to the on-board computer.

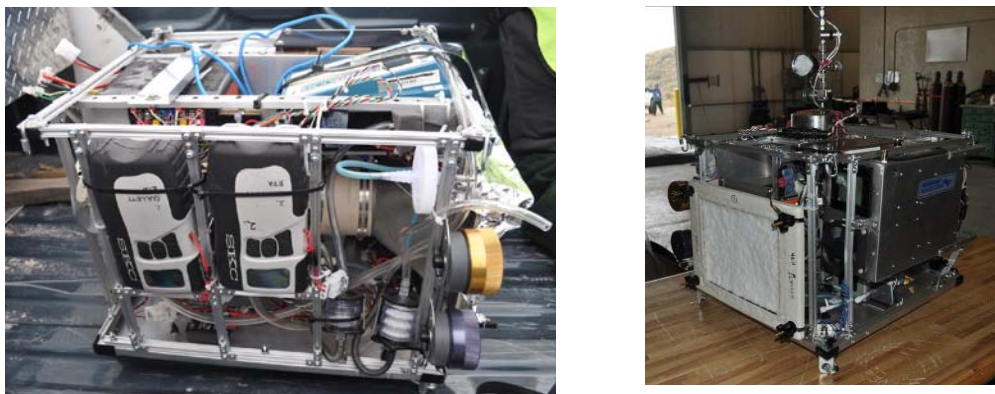


Figure 2-3. Two views of the Flyer with computer and wireless transmission.

2.3 Testing and Sampling Procedure

The Flyer was prepositioned downwind or in some cases straight above the propellant burn site with the aid of wind socks. The two vehicles equipped with electric winches and tethers were used to anchor and maneuver the Flyer. Vehicle drivers and all campaign participants were required to stay outside the safety zone away from the OB pans. The propellant burns were ignited one by one when winds blew towards the prepositioned Flyer. When necessary, the Flyer was maneuvered into the plume by reeling the tethers in or out, as guided by visual observations. The six to ten burn pans on the concrete pad contained 185-397 lb [84-180 kg] each of propellant (Table 2-2). The burn pans were positioned in two rows with three pans in each row for M31A1E1 propellant and two rows with two pans in each for M26 and SPCF propellant. When backup pans were available they were often prefilled with propellant to reduce the time between pan setups, (Figure 2-4).

The procedure for sampling the plumes of the static rocket firing tests at the Production Range was only different in that no personnel were located at the winch controls during the burns. The aerostat and Flyer were prepositioned downwind inside the personnel safety distance. Personnel were evacuated to an observation bunker about 1/3 of a mile (~0.5 km) distance from the rocket motors, where the winches could be remotely controlled to optimize the location of the aerostat within the plume. Upwind personnel were in radio contact to guide the position of the aerostat with respect to the plume. The test matrix and sampled analytes are shown in Table 2-2.

Table 2-2. Test matrix.

Date	Propellant	Pans x Charge size (lb)	VOC	SVOC	PM ₁₀	PM _{2.5}	HCl	Perchlorate	Continuous PM _{2.5}
3/22/2011	M31A1E1	6×212	X	X	X	X			
3/23/2011	M31A1E1	16×212	X	X	X	X			
		2×318	X	X	X	X			
		1×185	X	X	X	X			
		6×318		X	X	X			
3/24/2011	M31A1E1	7×344.5		X	X	X			X
		2×371		X	X	X			X
		1×397		X	X	X			X
3/26/2011	M26	14×333	X	X	X	X			
3/28/2011	M26	6×333	X	X	X	X			
		2×330	X	X	X	X			
3/29/2011	M26	18×333	X	X	X	X			
		2×322	X	X	X	X			
3/30/2011	M26	9×333		X	X	X			
		1×322		X	X	X			
3/31/2011	SPCF	9×220	X	X	X	X			
4/01/2011	SPCF	7×220	X	X	X	X			
		23×220		X	X	X			X
4/04/2011	SPCF	7×220		X	X	X			X
4/04/2011	Ambient air		X	X	X	X	X	X	
4/06/2011	AP, Sparrow rocket motor	12×133	X	X	X		X	X	

X = sampled.

**Figure 2-4. Concrete Burn Pad with six (left) and four (right) reusable burn pans.**

2.4 Emission Sampling and Analysis Methods

2.4.1 Carbon Dioxide by NDIR CEM and Carbon Monoxide by Electrochemical Cell

Carbon dioxide measurements were performed using a LI-COR Biosciences LI-820 non-dispersive infrared (NDIR)-based CEM mounted on the Flyer. The LI-CORs use a 14 cm optical bench, giving an analytical range of 0-20,000 ppm, with an accuracy specification of <2.5% of

reading. The instrument was preceded by a filter for particulate matter removal prior to the optical lens. Signal averaging was set to 2 seconds per reading. The LI-COR Bioscience LI-820 CEM was calibrated for CO₂ on a daily basis according to USEPA method 3A (USEPA 2008) using a zero gas (100 % nitrogen), span gas (4500 ppm CO₂), and gases of intermediate CO₂ concentrations (400 and 1500 ppm).

Carbon monoxide was sampled continuously using a semi-real time monitor. An onboard CO sensor (Creative Solutions RCO1000) measured CO concentration by means of an electrochemical cell through CO oxidation. Output is linear from 0 to 1000 ppm at an operating relative humidity range of 15-90%. The RCO 1000 was calibrated in the USEPA Metrology Laboratory prior to trip departure at 0 to 80 ppm with +/- 2 ppm error using USEPA method 3A (USEPA 2008). CO measured by flow through the chemical cell was corroborated by the measurement of a sample taken from the Summa canister system and analyzed via gas chromatography.

2.4.2 Summa Canister Sampling for Volatile Compounds, Carbon Dioxide, and Carbon Monoxide

2.4.2.1 Sampling Method

Summa canisters (1 L capacity) were used for collection of volatile organic compounds (VOCs) via USEPA Method TO-15 (USEPA 1999a). Canisters were obtained from a commercial laboratory (Columbia Analytical Services - CAS) that could analyze for target analytes at low limits of detection. An electronic solenoid valve sampling system atop the Summa canister was opened and closed by the CO₂ concentration trigger circuit at operator-set levels. An electronic pressure transducer and a pressure gauge was attached to the Summa canister which provided information on the status of the summa canister (i.e. empty, filling, or full) and the voltage equivalent of the Summa canister pressure was recorded on the onboard computer. The valve was followed by a 15 µm frit filter in the stem of the Summa canister resulting in an approximate sampling time of 15 seconds.

Prior to deployment, the Summa canisters were checked at the USEPA metrology laboratories for valve function (opening and closing) and sampling time. Prior to each experiment, the Summa canister electronic valve functioning was checked to see if it opened and closed properly.

2.4.2.2 Analytical Method

The volatiles were analyzed using USEPA Method TO-15 (USEPA 1999a) with selective ion monitoring mode GC/MS. A 0.4 L aliquot was pulled from the Summa canister and analyzed. An internal spiking mixture was added to the Lab control sample. All surrogate standard recoveries were within the method acceptance criteria of the CAS laboratory, e.g. the surrogate standard recovery for benzene was 88% which was within its method acceptance criteria of 66-103%.

Each Summa canister sample was also analyzed for carbon dioxide and carbon monoxide by GC, utilizing USEPA Method 25C (USEPA 1996), in which an aliquot of the collected Summa canister sample was injected into a sample loop equipped GC/FID. The CO₂ and CO surrogate stand-

and recoveries were 91 and 98 %, respectively, which are within the method acceptance criteria of the CAS laboratory: 71-123% and 73-132%, respectively.

The data were background-corrected (BC) by subtracting the ambient air contribution to the sample:

$$BC\ Analyte_i = Sample_{Analyte_i} (\mu g/m^3) - Ambient\ air_{Analyte_i} (\mu g/m^3)$$

2.4.3 Semi-Volatile Compounds

2.4.3.1 Sampling Method

Semi-volatile organics were sampled via USEPA Method TO-13A (USEPA 1999b) using a PUF/XAD-2 resin/PUF sorbent. The target analytes were the 16 EPA prioritized polyaromatic hydrocarbons (PAHs), nitrobenzene, and nitrotoluenes. The pre-cleaned XAD-2 resin sorbent was further cleaned at USEPA by solvent extraction with dichloromethane and drying with nitrogen to minimize contamination of the sorbent with the target analytes. This sorbent was delivered to the test site already mounted in the glass cartridge and was then inserted behind the fan. The sorbent was prepared for sampling by removing it from its shipping container, removing the aluminum foil wrapping, and inserting it in a cartridge holder mounted on a Windjammer brushless direct current (BLDC) blower (AMETEK). Semi-volatile sampling was performed using a BLDC low voltage blower for a nominal sampling rate of 0.65 m³/min. The blower was controlled by the CEM CO₂ trigger circuit or started from the ground via wireless control. Flow rate was measured by the pressure differential across a calibrated venturi. The venturi is a carefully calculated and constructed constrictor made and calibrated at the USEPA shop and Metrology Laboratory, respectively. As used here, it was mounted on the outlet of the BLDC semi-volatile sampler. A venturi has the property that fluid pressure through a constricted section of pipe is reduced. The fluid velocity must increase through the constriction to satisfy the equation of continuity, while its pressure must decrease due to conservation of energy. As such, a measurement of ΔP between the venturi's inlet and constricted diameter body was used to calculate flow rate. In practice, a calibration curve was developed from ΔP and actual flow measurements. The voltage equivalent to this pressure differential was recorded by the data acquisition system. The USEPA Metrology Laboratory performed these measurements using the venturi's matched transducer and data acquisition computer with a Roots meter. Following sampling, the glass cartridge (sorbent) was removed from the Flyer, wrapped in clean aluminum foil in order to seal the ends, returned to its shipping container, labeled, and stored at 4°C until delivered to the laboratory.

2.4.3.2 Analytical Method

The semi-volatile PUF/XAD-2 resin/PUF samples were prepared for analysis by solvent extraction with dichloromethane and then concentration by solvent evaporation. An internal standard, d8-naphthalene and other standards, were added to the sorbent before the sample was collected (Table 2-3). A deuterated recovery standard, D10-pyrene, was added before mass analysis. The internal standard recoveries were measured relative to the recovery standard and are a measure of the sampling train collection efficiency. Samples were analyzed utilizing full-scan mode. All in-

ternal standard recoveries were between 46 and 132% (D8-Naphthalene was between 50 and 85%).

Table 2-3. PAH surrogates, composition and purpose.

Spiking Solution	Analytes	Special Notes
PAHs - Internal Standards	D8-Naphthalene, D10-Acenaphthene, D10-Phenanthrene, D12-Chrysene, D12-Perylene	Added to sorbent prior to shipment to field
Recovery	D10-Pyrene	Added before mass analysis

Trip and field blanks were collected and analyzed. The trip blank was taken from the laboratory to the test site and returned to the laboratory unopened. The field blank was used for sampling ambient air to determine background concentrations. Both samples were analyzed for levels of target analytes and used to calculate the emission factor. The data were background-corrected (BC) according to:

$$\text{Ambient air Analyte}_i \text{ (ng/m}^3\text{)} = \frac{\text{Ambient air}_{\text{Analyte}_i} \text{ (ng/sandwich)} - \text{Trip blank}_{\text{Analyte}_i} \text{ (ng/sandwich)}}{\text{Ambient air Sampling volume (m}^3\text{)}}$$

$$\text{BC Analyte}_i = \frac{\text{Sample}_{\text{Analyte}_i} \text{ (ng/sandwich)} - \text{Trip blank}_{\text{Analyte}_i} \text{ (ng/sandwich)}}{\text{Sample Sampling volume (m}^3\text{)}} - \text{Ambient air}_{\text{Analyte}_i} \text{ (ng/m}^3\text{)}$$

2.4.4 Particulate Matter and Metals

2.4.4.1 Sampling Method

PM_{2.5} and PM₁₀ were sampled simultaneously using two size selective impactors (SKC, USA) with 47 mm tared Teflon filters (2 µm pore size) each with a SKC Leland Legacy sample pump with a constant airflow of 10 L/min. The internal flow sensor measured flow directly and acted as a secondary standard to constantly maintain the set flow. The volume display was continually updated, based on corrected flow rate multiplied by sampling time. The pump operation was controlled by the CEM CO₂ trigger circuit or wireless-started from the ground. The SKC Leland Legacy Sample pump was calibrated during the sampling campaign with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA), which is a primary standard airflow calibrator.

2.4.4.2 Analytical Method

The filters were obtained from a commercial laboratory (CHESTER LabNet) that could provide tared filters and analyze for target metal analytes at low limits of detection. PM was measured gravimetrically as the difference between final and tare masses for each filter. The weighing of the filters followed the procedures described in (40 CFR Part 50, 1987). Calibration for determining mass of conditioned media was performed as described in Quality Assurance Guidance Document 2.12 (USEPA, 1998). The PM collected on Teflon filters was also used to determine concentrations of target metals: Pb, Ba, Al, K, Fe, and Mo. The metal analysis was determined by inductively coupled plasma according to USEPA Compendium Method IO-3.4 (USEPA,

1999c). An internal spiking mixture of the target compounds was added to the Chester control sample. All surrogate standard recoveries were 83-111% which was within the method acceptance criteria (80-120%). Ash from M31A1E1, M26, and SPCF was collected and analyzed for the target metals.

2.4.5 Continuous PM_{2.5}

During some M31A1E1 and SPCF propellant burns, the PM_{2.5} concentration of the plume was continuously determined by a DustTrak 8520 on the aerostat. This instrument measures light scattering by aerosols as they intercept a laser diode. The aerosol concentration range for the DustTrak was 0.001-100 mg/m³ with a resolution of $\pm 0.1\%$ of reading, at a wind speed of 0-22.5 mph (0-10 m/s). Sampling time was set to every second at a flow rate of 1.7 L/min. The addition of the DustTrak was opportunistic due to a loan of the instrument and was not part of the original measurement plan.

2.4.6 Perchlorate, Chlorate, and HCl

2.4.6.1 Sampling Method

Perchlorate (ClO₄⁻) and chlorate (ClO₃⁻) were sampled using a modified method from (Lamm et al., 1999). The method consisted of sampling at a flow rate of 4 L/min through a 37 mm diameter mixed cellulose ester (MCE) filter (0.8 μ m pore size) enclosed in a closed-face cassette (SKC Corporation). Perchlorate, chlorate, and chloride salts were captured as a solid on the filter, which assumes no perchloric acid formation. HCl was sampled in parallel by two different methods, as shown in Figure 2-5:

1. Alkali-impregnated filter according to ISO Method 21438-2 (International Standard, 2009).
2. Silica gel collection according to NIOSH Method 7903 (U.S. NIOSH 1994).

Methods for sampling HCl are primarily derived from those intended for sampling inhalable HCl to relate to exposure risk. Silica gel collection methods may undersample HCl mist, as particle size collection characteristics on the silica gel sorbent tube do not match the inhalable convention (Howe, et al 2006). Although there are unanswered questions about the relevance of these methods for the inhalable particle/droplet size (Howe, et al 2006), we were interested in efficient capture and quantification. HCl was sampled in parallel using alkali-impregnated filters following the perchlorate filter and silica gel tubes (Lindsay et al. 1999). HCl gas is expected to pass through the perchlorate/chloride salt filter and be adsorbed by a second, quartz filter coated with Na₂CO₃. These coated filters are available in a cartridge from SKC Corporation. Any hydrochloric acid transiently collected on the initial filter is expected to rapidly evaporate and be collected along with the gaseous HCl (Howe, et al 2006). This method, including a prefilter followed by a Na₂CO₃-impregnated quartz filter, is consistent with a method from France (Institut National de Recherche et de Sécurité 2002) as cited in (Howe, et al 2006), which became a European standard method 2009 (International Standard 2009).

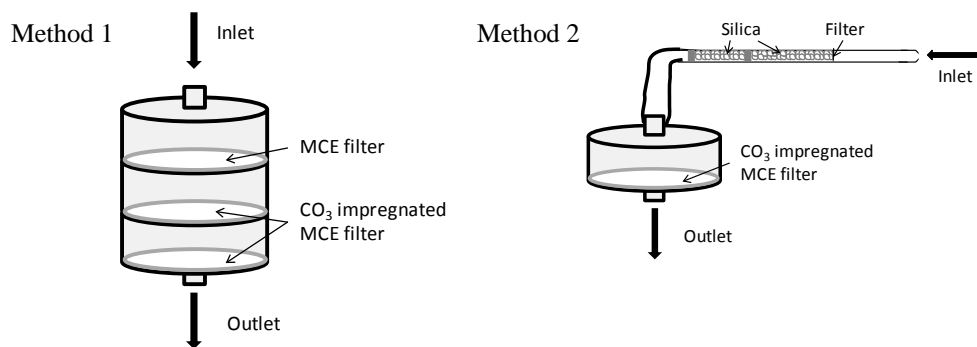


Figure 2-5. Sampling apparatus for HCl, perchlorate, chlorate, and chloride salts. Filter method 1 (ISO 21438-2) followed by an additional CO₃ filter at the left, and silica gel method 2 (NIOSH 7903) followed by a CO₃ filter at the right.

2.4.6.2 Analytical Method

Cassette samples and the pre-filter in the silica tube were dissolved/extracted in water, an internal standard added, and the solution analyzed for perchlorate with LCMS and chloride with ion chromatography as per USEPA Method 6850 (USEPA 2007). Samples were analyzed at Columbia Analytical Services (CAS, NY). The perchlorate prefilter and Na₂CO₃ filter both were analyzed for target analytes prior to sampling at Tooele in order to establish their potential contamination levels. Ambient air background levels were determined for perchlorate, chloride, and HCl. The chloride concentration on the MCE CO₃ filter and the silica were multiplied by a factor of 1.0284 in order to convert from anion (Cl⁻) to acid concentration (HCl) (International Standard, 2009).

2.4.7 Sampling Time

The sampling time for the semi-volatile sorbent, PM₁₀ and PM_{2.5} filter, HCl, and perchlorate filter/silica were all initiated with the same trigger circuit. The durations, therefore, were identical and the cessation of sampling was based upon the CO₂ concentration falling back below the trigger level since this lowering of the CO₂ concentrations indicate the passage of the plume. The sampling duration was different for the Summa canister since it was initiated with a separate CO₂ trigger concentration. A higher CO₂ trigger was used for the Summa canister to insure that sample was gathered near the peak concentration of the plume. When the canister filled to approximately 80%, it would cease to collect sample.

2.4.8 Calculation of Emission Factors

Values of CO₂ concentration from the CEM and Summa canisters were used to calculate a co-sampled carbon concentration, permitting conversion of analyte concentrations to emission factors by the carbon mass balance method. In this method, the ratio of the sampled target analyte concentration to the total sampled carbon (represented by CO₂) is related back to the initial ordinance weight through knowledge of the carbon concentration/carbon fraction in the original ordinance and the assumption of 100% oxidation of the carbon. In all emission factors, the background concentration of the target analyte, determined from Flyer-based instruments and ground-based upwind instruments, is subtracted from the measured amount.

Emission factors were calculated according to (AP-42 2009):

$$EF_i = f_c \times \frac{Analyte_{ij}}{C_j} \quad \text{where:}$$

EF_i = Emission Factor for target analyte i (lb/lb NEW).

f_c = mass fraction of carbon in the ordnance.

$Analyte_{ij}$ = background-corrected concentration (lb analyte/ft³) of the target analyte i collected from the volume element j of the plume.

C_j = background-corrected concentration of carbon (lb C/ft³) collected from volume element j of the plume (carbon calculated from CO₂ from either the CEM or the Summa canister).

Likewise, environmental fate factors (16), which yield the fraction of conserved species present in the emissions compared to that present in the ordnance were calculated:

$$EFF_i = \frac{f_c}{f_i} \times \frac{Analyte_{ij}}{C_j} \quad \text{where:}$$

EFF_i = Environmental Fate Factor for target analyte i (emissions analyte I in lb/lb i in ordnance).

f_c = mass fraction of carbon in the ordnance.

f_i = mass fraction of analyte i in the ordnance

$Analyte_{ij}$ = background-corrected concentration (lb analyte/ft³) of the target analyte i collected from the volume element j of the plume.

C_j = background-corrected concentration of carbon (lb C/ft³) collected from volume element j of the plume (carbon calculated from CO₂ from either the CEM or the Summa canister).

3. Results and Discussion

The Flyer successfully sampled emissions from 94% of the 139 open burns of propellant and 92% of the 12 static fires (Figure 3-1), as determined by the number of times that the CO₂ concentration exceeded the ambient air CO₂ concentration. Each measured exceedance of the ambient CO₂ concentrations was referred to as a “hit.” “Misses” were due to unanticipated plume paths, primarily due to wind shifts. The average in-plume sampling time was approximately 22 seconds for OBs and 7 seconds for the static fires (Table 3-1). The OB hits are slightly higher than in 2010 while the ΔCO₂ values are similar (Table 3-1). The total number of samples collected for each propellant is shown in Appendix D.

Table 3-1. Sampling summary.

	M31A1E1	M26	SPCF	AP Sparrow Rocket Motor	M1 (2010)
No. of burns	41	52	46	12	60
No. of hits	40	47	43	11	51
Hits (%)	98	90	93	92	85
Avg. plume sampling time (s)	24	19	23	7	18
ΔCO ₂ (ppm)	494	505	421	104	463



Figure 3-1. Open burns of A) M31A1E1, B) M26, C) SPCF, and D) static fire of Sparrow rocket motor

3.1 Carbon Dioxide and Carbon Monoxide

The highest in-plume CO₂ concentrations obtained for each of the studied propellants are shown in Figure 3-2. No CO was detected using the semi-continuous electrochemical cell for any of the propellants. This was likely due to the short sampling time in each plume, the minimal CO concentration present, and the long response time required for the cell (~90 seconds) relative to the duration of the sampler in the plume.

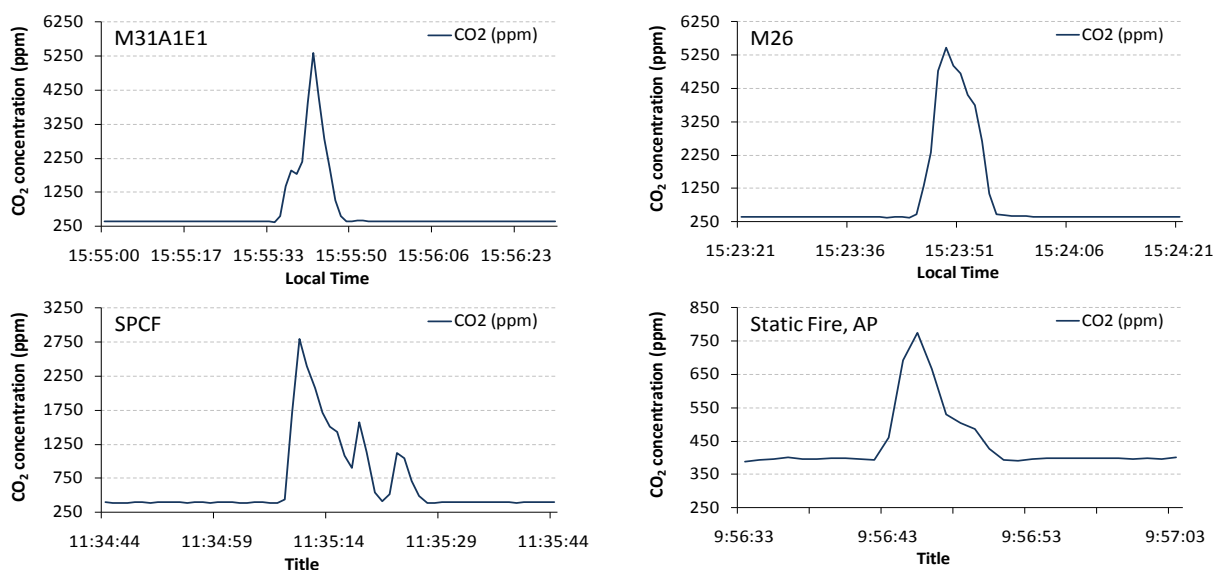


Figure 3-2. In-plume CO₂ concentration traces (uncorrected for ambient) for each of the propellants.

3.2 Summa Canister Sampling for Volatile Compounds, Carbon Dioxide, and Carbon Monoxide

The short plume residence times for the Flyer meant that multiple plume samples were necessary in order to fill the Summa canister with a composite sample. The improved Summa canister sampling valve (from that used in 2010) worked well as shown by Figure 3-3, i.e. the valve turned on and off at the set CO₂ trigger level and no leaks occurred between openings. The average delta CO₂ concentrations as well as VOC emission factors are shown in Table 3-2. In general good agreement is noted for VOC values with 2011 and 2010 reported levels. However, none of the three Summa canister samples of the SPCF had detectable levels of benzene (detection limit 0.56 µg/m³). Agreement for trace organic concentrations between the propellants was quite good, lending confidence in the methods. No CO was detected in any of the Summa canisters (MRL = 8 ppm), perhaps due to the small sample size. Very low levels of CO would be expected with complete combustion of the propellants. Benzene and several other compounds from the ambient

air background samples were below detection limits¹ in this year's sampling. A smaller (1 L) Summa canister was used for WP-2153 than the 6L one used for WP-1672. The smaller sampling volume may have limited our ability to detect these trace compounds even at high CO₂ concentrations in the plumes. Results for each summa canister collected for each propellant is shown in Appendix D.

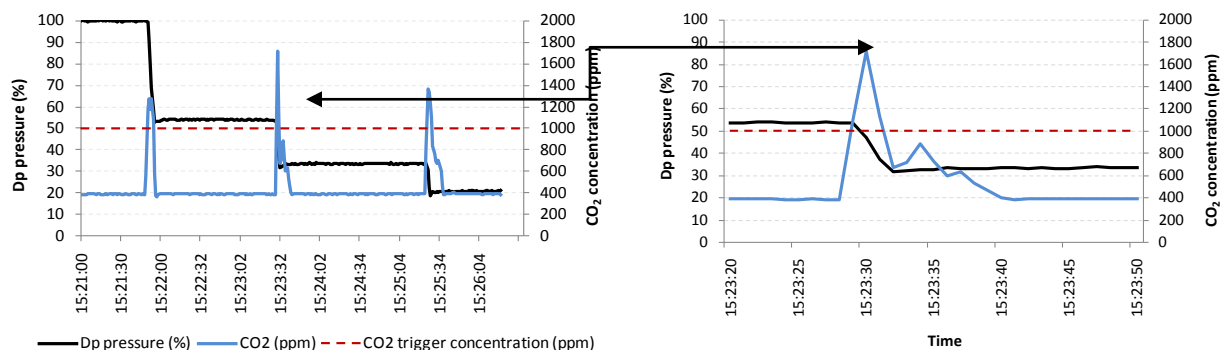


Figure 3-3. The Summa canister pressure (Dp) decreases when the valve is open at the CO₂ concentration above or equal to the 1000 ppm trigger level and the Dp is stable between plumes (no leak).

Table 3-2. VOC sampling results and average emission factors.

	M31A1E1	M26	SPCF	AP Sparrow Rocket Motor	M1 (2010)
ΔCO_2 (ppm)	403	678	427	20	452
STDV (ppm)	195	757	243	NA	537
CO (ppm)	ND	ND	ND	ND	NS
Benzene (lb/lb Carbon)	1.1E-05	1.1E-05	ND	ND	1.6E-05
Toluene (lb/lb Carbon)	2.3E-04	6.7E-06	4.2E-06	4.1E-05	1.8E-06
Ethylbenzene (lb/lb Carbon)	2.2E-05	9.8E-06	8.7E-06	ND	1.4E-06
Xylene (lb/lb Carbon)	1.3E-04	2.5E-05	4.1E-05	1.1E-04	3.8E-07
1,2,4-Trimethylbenzene (lb/lb Carbon)	3.4E-05	1.4E-05	4.3E-05	5.6E-05	NS

* ND – Not detected, ND values were ignored when calculating the emission factor. NA – Not applicable. NS – Not sampled. (NOTE – Changed ethylbenzene SPCF value should be 8.7E-06 based on Table D8)

3.3 Semi-Volatile Compounds

SVOC results are shown in Table 3-3. Due to the short sampling duration of each burn, multiple events were used to create single, composite samples for semi-volatiles (PUF/XAD-2 resin/PUF). These single samples were obtained by reusing the same sorbent media during multiple

¹ Detection limit – the minimum concentration at which an analyte can be detected above the instrument's background noise

sequential events. Two semi-volatile composite samples were collected from each propellant for OB and one from static fire. The ambient air concentrations were at the same level as last year and the plume concentrations were at least five times higher than the ambient air concentrations. Results for each SVOC sample collected for each propellant are shown in Appendix D.

Table 3-3. PAH Emission Factors in lb/lb Carbon*.

Compound	M31A1E1 lb/lb Carbon	M26 lb/lb Carbon	SPCF lb/lb Carbon	AP Sparrow Rocket Motor lb/lb Carbon	M1 (WP-1672) lb/lb Carbon
Nitrobenzene	4.0E-06	1.4E-07	ND	ND	NS
Nitrotoluenes	2.1E-07	ND	ND	ND	NS
Naphthalene	6.7E-06	1.2E-07	1.0E-07	8.4E-07	2.8E-07
Acenaphthylene	2.1E-07	2.9E-08	2.1E-08	5.3E-08	3.2E-08
Acenaphthene	1.2E-07	8.5E-08	9.3E-09	ND	ND
Fluorene	5.9E-07	3.3E-08	3.1E-08	1.6E-07	2.5E-08
Phenanthrene	6.1E-07	6.2E-08	1.0E-07	5.5E-07	ND
Anthracene	4.8E-08	3.8E-09	7.4E-09	5.7E-08	ND
Fluoranthene	8.2E-08	1.7E-08	2.0E-08	1.9E-07	ND
Pyrene	6.4E-08	1.2E-08	1.6E-08	ND	ND
Benzo(a)anthracene	ND	ND	ND	ND	ND
Chrysene	ND	ND	9.3E-09	ND	ND
Benzo(b)fluoranthene	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND
Benzo(ghi)perylene	ND	ND	ND	ND	ND

* ND – not detectable. The number of values that derived each EF is shown in Appendix D.

3.4 Particulate Matter and Metals

Multiple burn events were used to create a single composite PM₁₀ and PM_{2.5} sample. Two PM₁₀ and PM_{2.5} filter samples were collected for each propellant, with the exception of M31A1E1 (three filters) and AP (a single filter, only PM₁₀). The propellant emission factors for PM₁₀ and PM_{2.5} were very similar (a maximum factor of 4) as were the coefficients of variance and relative percent difference as shown in Table 3-4. This suggests that the majority of the mass was less than 2.5 µm in size (PM₁₀ mass includes PM_{2.5}) and also shows the reproducibility of the method and the similarity between propellants. The PM₁₀ emission factor for the propellants studied this year was similar to last year's propellant (M1), Figure 3-4, suggesting relative consistency between propellants undergoing OB. The Sparrow rocket motor (AP propellant) had the highest PM₁₀ emission factor.

The metal emission factors are shown in Table 3-5. About 80% of the Pb in SPCF was accounted for by the PM₁₀ plume sample and, since the values for PM₁₀ were virtually the same as PM_{2.5}, virtually all of the captured Pb was in the fine PM fraction. The same conclusion can be drawn for Ba in M26. For the Sparrow rockets, the Al environmental fate factor shows that only 16% of it was accounted for by the PM₁₀ plume sample (literature BangBox® data show this value to be only 5.5%) (AP-42 2009). This may suggest that either particles larger than PM₁₀ were formed or that the PM segregated from the CO₂ in the plume prior to reaching the sampler. In either case, these particles would not have been collected by the PM₁₀ sampler. Results for each PM sample collected for each propellant are shown in Appendix D.

Table 3-4. Emission factors for PM₁₀ and PM_{2.5} in lb/lb NEW.*

	M31A1E1	M26	SPCF	AP Sparrow Rocket Motor	M1 (2010)
PM ₁₀	4.0E-03	1.1E-02	1.4E-02	1.5E-01	5.7E-03
CV/RPD	12	2	5		
PM _{2.5}	3.6E-03	1.1E-02	1.5E-02	NS	NS
CV/RPD	11	11	1		

Table 3-5. Emission factors for metals in lb/lb metal*

	M31A1E1	M26	SPCF	AP Sparrow Rocket Motor	M1 (2010)
K (PM ₁₀)	0.16	0.67	0.53	NS	NA
CV/RPD	13	3	9		
K (PM _{2.5})	0.15	0.67	0.53	NS	NS
CV/RPD	14	3	7		
Ba (PM ₁₀)	NA	0.67	NA	NA	NA
RPD		1			
Ba (PM _{2.5})	NA	0.64	NA	NS	NS
RPD		1			
Pb (PM ₁₀)	NA	NA	80	NA	0.55
RPD			5		
Pb (PM _{2.5})	NA	NA	0.78	NS	NS
RPD			5		
Al (PM ₁₀)	NA	NA	NA	0.16	NA
Fe (PM ₁₀)	NA	NA	NA	1.19	NA
Mo (PM ₁₀)	NA	NA	NA	1.68	NA

* CV – coefficient of variance (only M31A1E1), RPD – relative percent difference (all others), NS = not sampled. NA – Not analyzed. The number of values that derived each EF is shown in Appendix D.

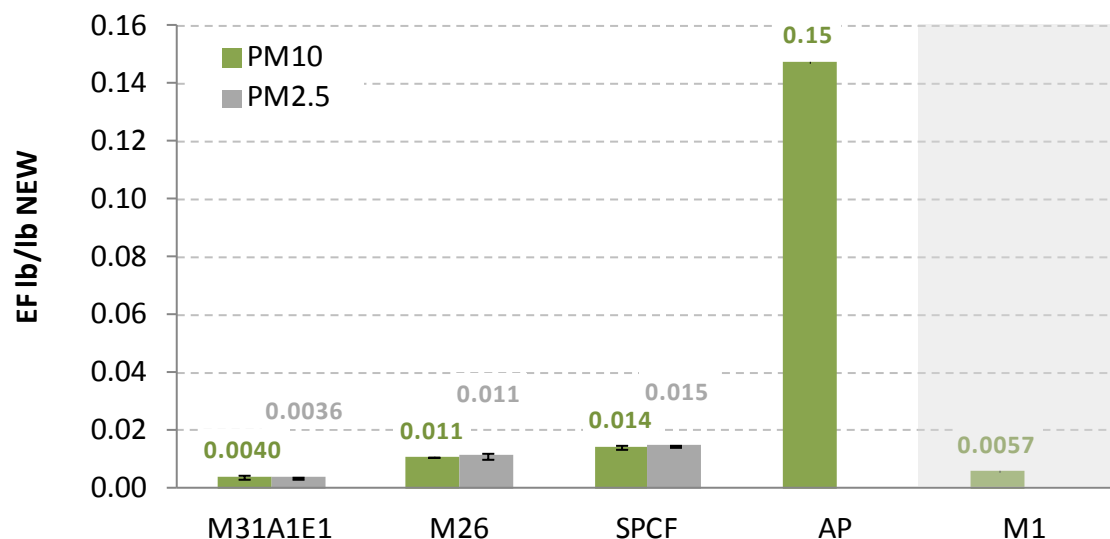


Figure 3-4. PM_{2.5} and PM₁₀ emission factors for the different propellants. Error bars denoted 1 STDV for M31A1E1 and relative difference for M26 and SPCF.

Depending on the propellant, about one third to virtually all of the K in the propellants are accounted for in the emission measurements. K also shows up in the Sparrow rocket samples despite the lack of K present in the propellant. This may be due to the general ubiquitousness of K in the environment.

While care was taken to sweep out the pans between propellants burns, the propellant residue (ash) was analyzed in order to establish any possible carryover of metals between propellants (Table 3-6). While K was present in all three propellants, its concentration in the ash does not increase throughout the testing (the propellants were tested in the order shown) indicating little propellant to propellant contamination. Some Ba carryover into SPCF from M26 seems to have occurred although the testing order was not specifically designed to evaluate carryover effects. In the future, this issue should be examined in more detail for OB.

Table 3-6. Metal content in propellant ash and percentage of metal in propellant.

	M31A1E1		M26		SPCF	
	Ash (mg/kg)	Propellant (%)	Ash (mg/kg)	Propellant (%)	Ash (mg/kg)	Propellant (%)
K	96900	0.56	43800	0.27	84100	0.45
Ba	6.8	NA	112000	0.39	13500	NA
Pb	151	NA	2790	NA	155000	0.78

3.5 Continuous PM_{2.5}

While not part of the original test plan, opportunistic continuous PM_{2.5} was measured for SPCF and M31A1E1 propellants. As shown in Figure 3-5 for SPCF, the CO₂ and PM_{2.5} traces followed each other suggesting consistency in the PM_{2.5} to CO₂ ratio. For some of the M31A1E1 burns, the combustion was poor at the start which resulted in a white, smoky plume. This initial smoky plume contained a much higher concentration of PM_{2.5} than the subsequent plume which was almost visually indiscernible. There is no clear reason for this difference. These two portions of the same plume are shown graphically and pictorially in Figure 3-6.

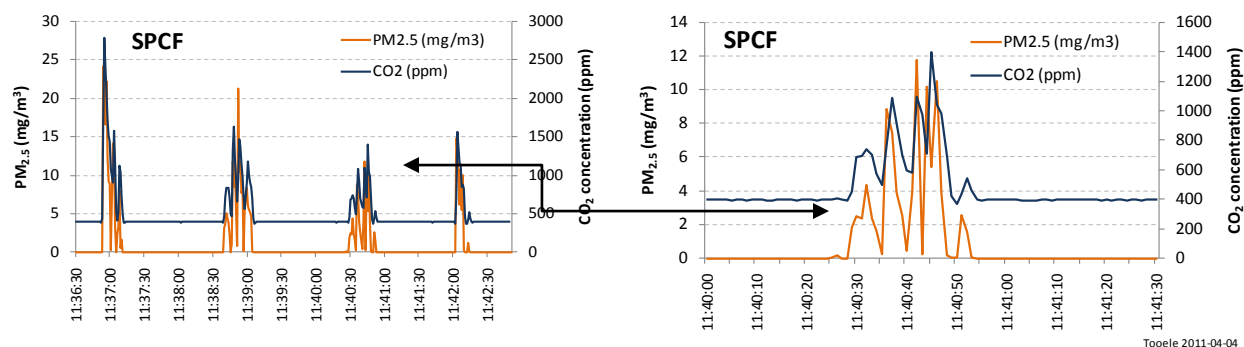


Figure 3-5. Continuous PM_{2.5} and CO₂ trace for SPCF propellant.

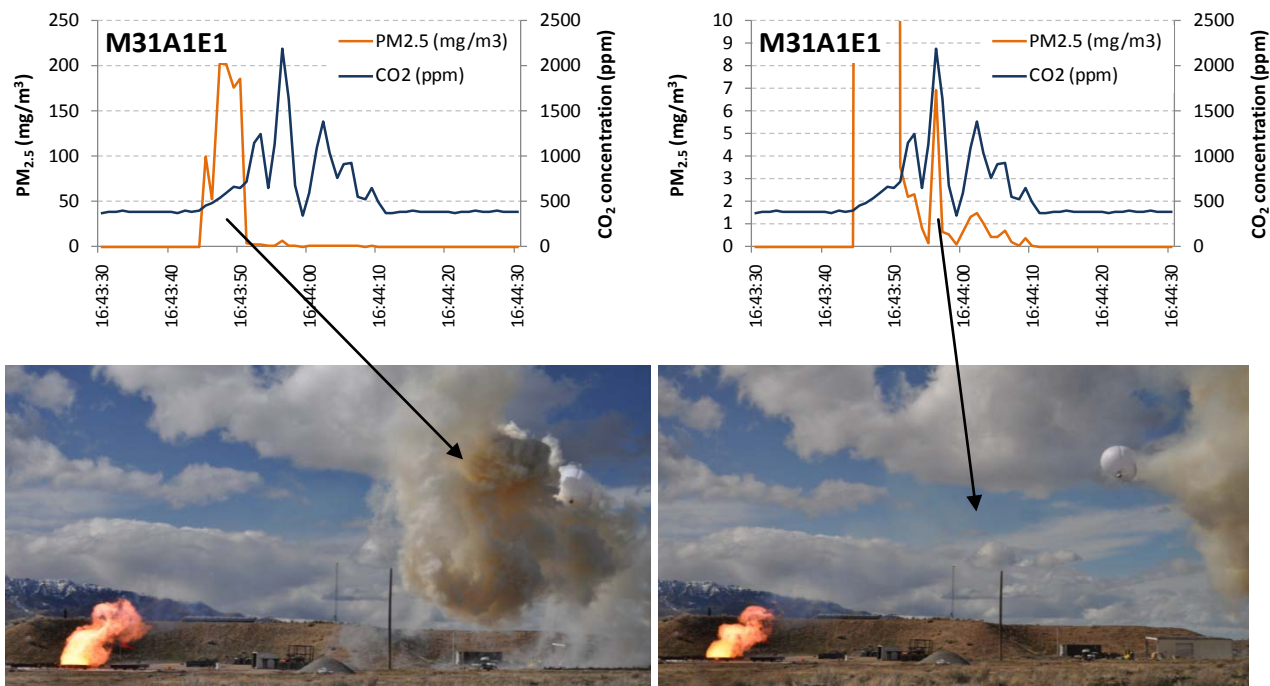


Figure 3-6. Continuous PM_{2.5} and CO₂ trace for a single M31A1E1 propellant burn with an initial smoky plume (left) and subsequent invisible plume (right).

Figure 3-7 plots the simultaneous continuous $\text{PM}_{2.5}$ and CO_2 concentration for one test of SPCF. The strong correlation suggests minimal variation between $\text{PM}_{2.5}$ and CO_2 throughout the plume; the PM and gas distribute rather consistently on average. The continuous $\text{PM}_{2.5}$ method compared reasonably well with the batch $\text{PM}_{2.5}$ values. The 7-plume SPCF $\text{PM}_{2.5}$ value from the DustTrak was 5.0 mg/m^3 , whereas the average of the M31A1E1 39-plume $\text{PM}_{2.5}$ values was 12 mg/m^3 .

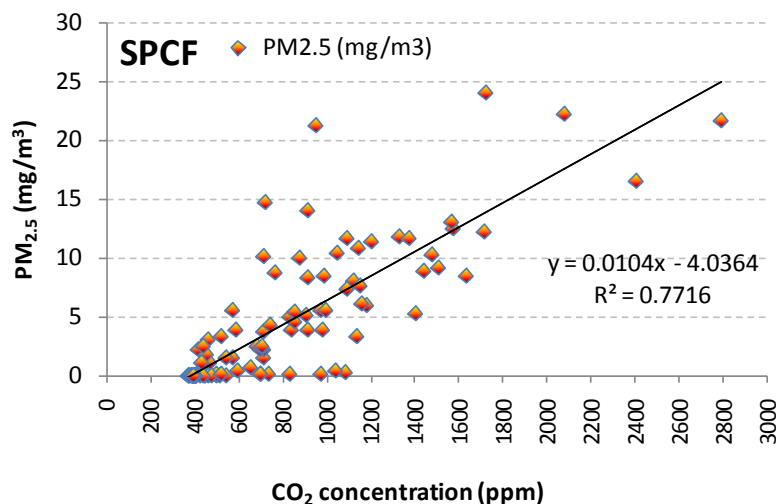


Figure 3-7. Continuous $\text{PM}_{2.5}$ and CO_2 concentration for one test of SPCF

3.6 HCl and Perchlorate

Two composite Cl samples were collected simultaneously from static firing of twelve Sparrow rocket motors containing AP propellant. The limited number of AP tests was due to the unavailability of propellant for pan burning. The Sparrow rocket motor firing was opportunistic at the nearby Production Range. Two Cl samples were analyzed, one for each of the two modified sampling methods (Figure 2-5):

1. Alkali-impregnated filter according to ISO Method 21438-2 (International Standard, 2009).
2. Silica gel collection according to NIOSH Method 7903 (U.S. NIOSH 1994).

For both of these methods, the last CO_3 filter in series had concentrations that were close to the MRL, which suggests that no breakthrough of chlorides occurred. The chloride concentration on the two first filters for method 1 and the silica gel for method 2 was ~ 10 times higher than the MRL. No perchlorate concentration was detected, however, chlorate was detected but it was very close to its MRL. Low levels of these emissions are expected with complete combustion of the propellants. HCl and chlorate ambient air concentrations were very low and close to the MRL even though the sampling time was 1-2 hours. The plume sample was only collected for 1 minute

but the HCl and chlorate plume concentrations were 1000 and 10 times higher than the ambient air concentrations, respectively.

Table 3-7 compares the HCl, perchlorate, and chlorate concentrations measured by the two sampling methods and Table 3-8 compares the EFs. The HCl concentrations in the plumes and resulting emission factors were very similar even though two different methods were used. Interestingly, only 15 to 19% of the propellant Cl was collected as HCl (Table 3-8). When the PM-bound chloride is added, the Cl environmental fate factor suggests that less than half of the Cl ends up in the plume. This is contrary to BangBox® data where over 90% of the Cl was detected as HCl. However, the BangBox® and static fire situations are very different fuel configurations and are probably not a good comparison. This is also the first time HCl was ever successfully sampled from a static fire (previous attempts by others failed to detect any HCl) and then only from a single static firing series. The limited Al recovery (16%) and Cl recovery suggest that the fate of these emission products need additional study.

Table 3-7. HCl, particulate chlorides, perchlorate, and chlorate concentrations from AP.*

Sampling method	Chlorides from particulates (mg/m ³)	HCl (mg/m ³)	HCl (ppm)	Perchlorate, ClO ₄ ⁻ (mg/m ³)	Chlorate, ClO ₃ ⁻ (mg/m ³)
Filter, ISO 21438-2	42	21	13	ND	0.0003
Silica, NIOSH 7903	ND	26	16	ND	ND
MRL	3.5	2		0.0005	0.0005

* ND – Not detected. MRL – Method reporting limit.

Table 3-8. HCl, perchlorate, and chlorate emission factors from AP.*

Sampling method	HCl	Perchlorate, ClO ₄ ⁻	Chlorate, ClO ₃ ⁻
Filter, ISO 21438-2 (lb/lb NEW)	0.034	ND	4.6E-06
Filter, ISO 21438-2 (lb/lb Cl)	0.15	ND	2.0E-06
Filter, ISO 21438-2 (lb/lb C) [#]	0.32	ND	4.9E-06
Silica, NIOSH 7903 (lb/lb NEW)	0.043	ND	ND
Silica, NIOSH 7903 (lb/lb Cl)	0.19	ND	ND
Silica, NIOSH 7903 (lb/lb C)	0.41	ND	ND

* ND – Not detected. [#]Values included for reference to the carbon balance method.

3.7 Emission Factors versus Literature Values

Table 3-9 compares this work's PM₁₀, benzene, naphthalene, Pb, and HCl emission factors with those from the literature. The PM₁₀ data for each propellant type are within a factor of 2 or 3, except for the M31A1E1 for which the literature value is 200 times higher than the Flyer value. This difference could depend on the burn behavior of M31A1E1 as shown in *Section 3.5*. The Pb environmental fate factors derived from this year's study (SPCF) and last year's study (M1) were also very similar (factor of 2).

Table 3-9. Emission factor comparison; derived emission factor ("Flyer Open Test Range") versus published emission factor (Literature Bang Box and Open Test Range) (AP-42 2009)

Propellant type	Propellant	Data source	Test type	PM ₁₀ (lb/lb NEW)	Benzene (lb/lb C)	Naphthalene (lb/lb C)	Pb EFF (lb/lb)	HCl EFF (lb/lb)
Single base	SPCF	Flyer	OTR	1.4E-02	ND	1.0E-07	8.0E-01	NS
	M1	Flyer	OTR	5.7E-03	1.6E-05	2.8E-07	5.5E-01	NS
	M1	Lit.	OTR	6.9E-03	1.4E-05	6.3E-08	BDL	NS
Double base	M26	Flyer	OTR	1.1E-02	1.1E-05	1.2E-07	NS	NS
	M9	Lit.	BB	1.6E-02	1.2E-05	BDL	NS	NS
	Double-base A	Lit.	BB	1.9E-02	BDL	BDL	6.3E-01	NS
Triple base	M31A1E1	Flyer	OTR	4.0E-03	1.1E-05	6.7E-06	NS	NS
	M31A1E1	Lit.	BB	9.1E-01	BDL	BDL	NS	NS
AP based composite	Sparrow rocket motor	Flyer	OTR	1.2E-01	ND	8.4E-07	NS	1.7E-01
	Al AP	Lit.	BB	4.2E-01	BDL	BDL	NS	9.4E-01

* OTR – open test range. BB – BangBox®. ND – Not detected. NS – not sampled. BDL – below detection limit. EFF – Environmental Fate Factor.

3.8 Open Detonation Trials

Initial trials of soil-covered OD without measurements were undertaken in order to understand the sampling challenges for future work. The soil-covered tests detonated either two or four anti-tank mines to understand the shrapnel fragmentation, soil debris, and pressure wave impacts on the aerostat. The two mine detonations used 50 lbs NEW and the four mine detonations used 100 lbs NEW. An ad hoc blast shield consisting of two or more 4 ft x 8 ft oriented strand boards and multiple sand-bag-laden pallets was placed 60 ft from the covered detonations (Figure 3-8). The blast shield separated the line of sight between the detonation and a 30 ft x 30 ft plastic tarp anchored to the ground 180 ft from the detonation site. The tarp served as the location marker for the aerostat that would be anchored to the ground before being released to the plume after detonation. The ad hoc blast shield protected the tarp from direct hits but debris falling in an arc, including stones and several pieces of hot shrapnel, hit the tarp. The indirect stones are likely inconsequential but the shrapnel was hot enough to melt through the plastic. A special fabric has

been identified which will likely serve as a tent or shroud to protect the aerostat on occasions when the aerostat is released after detonations.



Figure 3-8. Covered detonation crater from a 50 lb NEW anti-tank mine detonation, ad hoc blast shield, and shrapnel/debris tarp (background, left, on ground).

3.9 Additional Methods Development

Testing of AP-based propellants in burn pans was precluded by the inability to obtain the propellant in time for testing. In lieu of that, opportunistic sampling was conducted at the Production Range for the static fire of AP-containing Sparrow rocket motors. This field sampling using the filter and silica gel methods was apparently successful, but only a single series of rocket motor firings were sampled (results are reported above). Further, the potential for breakthrough of the analytes could not be assessed. Additional laboratory work was identified to allow methods development with parallel samplers, control of flow rates, sample size, and simultaneous methods evaluation. Work on HCl testing will be done in 2011 at the USEPA facilities at Research Triangle Park and small charge (5-25 g) AP burns will be done at the U.S. Navy's Naval Surface Warfare Center in Indian Head, Maryland. This work is only for method development and is intended to provide a source of the target analytes but is not meant to simulate the actual field combustion process. Additional field work with static firing of AP-containing propellants seems necessary to clarify the very low Cl and Al balance.

4. Conclusions

Overall, the study was successful in determining the feasibility of the deployed measurement systems. The field campaign and its data analysis results clearly indicated that many of the deployed systems can become powerful tools to characterize air emissions from field OB operations.

Emissions were successfully collected from OB in pans of three propellant types (M31A1E1, M26, and SPCF) and static firing of Sparrow rocket motors containing AP. The sampling method consisted of positioning an aerostat-lofted instrument and sampling apparatus into the burn plume. The Flyer sampling package included measurements of CO₂ and CO, co-sampled PM₁₀ and PM_{2.5}, metals, HCl, perchlorate, chlorate, volatile organic compounds, and semi-volatile organic compounds, allowing determination of emission factors based on the propellant weight. The Flyer successfully sampled emissions from 94% of the 139 open burns of propellant and 92% of the twelve static fire events. The resulting emission factors for PM₁₀ and PM_{2.5} from OB were very close for each propellant suggesting that PM generated from OB is mostly fine particulate matter (PM_{2.5}). The PM₁₀ and PM_{2.5} emission factors were also similar to each other for the single, double, and triple base propellants, whereas the PM₁₀ emission factor from the static fire of rocket motors (AP propellant) was about 10-fold higher than propellant OB in pans. The derived emission factors of Pb and Ba from SPCF and M26, respectively, were in the same range as the Pb emission factor from the WP-1672 study of M1 propellant. Methods based on indoor air and personal samplers were employed to measure Cl species with two different sampling methods; results from both methods were similar. Preliminary results suggest that the methods are working. While HCl was successfully sampled for the first time from a static fire, the Cl recovery did not agree with BangBox® values, likely due to propellant differences. Chlorate was also detected but was very close to the method reporting limit. No perchlorate and CO were detected for any of the propellants. Only a very limited number of static fire events were sampled and additional work is necessary to close material balances for Cl and Al. Lastly, trial detonation tests identified the potential safety issues and strategies for air characterization from soil-covered detonations.

All test plans and reports have been provided to the Joint Ordnance Commanders Group Demil Subgroup Chairman for appropriate coordination within DoD and EPA as dictated in the Open Burning Open Detonation Emissions Factor Protocol (Joint Conventional Ammunition Policy and Procedure #7). Data obtained from this study will greatly assist DoD in performing health risk assessments and obtaining permits for their OB/OD operations.

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Appendix A: USEPA Quality Assurance Project Plan



Imagine the result



Determination of Emission Factors from Open Burning and Open Detonation of Military Ordnance

Quality Assurance Project Plan
Category IV / Proof of Concept

Revision 0.1

Work Assignment 0-52

January 2010



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**Determination of Emission Factors
from Open Burning and Open
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Quality Assurance Project Plan
Category IV / Proof of Concept
Revision 0.1

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**Determination of Emission Factors
from Open Burning and Open
Detonation of Military Ordnance**

Version 0.1

Date: January 2010

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1. Project Description and Objectives

This Quality Assurance Project Plan (QAPP) provides guidance to personnel conducting emission testing under the U.S. Environmental Protection Agency (EPA) Work Assignment (WA) entitled "*Determination of Emission Factors from Open Burning and Open Detonation of Military Ordnance*", Contract Number EP-C-09-027, WA Number 0-52, Project Number RN99270.0052. This work is funded in part by an Intergovernmental Agreement (IA) which provides funding through the Strategic Environmental Research and Development Program (SERDP).

This WA is designed to develop and apply methods for sampling Open Burning/Open Detonation (OB/OD) of military ordnance in the field to characterize gaseous and particulate matter (PM) emissions for determination of emission factors of various target compounds. This project will use a novel measurement approach consisting of an aerial, balloon-borne instrument developed by EPA ("The Flyer").

This document covers in detail the background, objectives, technical approach, quality assurance (QA), and quality control (QC) aspects of data collection and analysis.

1.1 Background

U.S. Department of Defense (DOD) Installations, especially demilitarization facilities and Army Ammunition Plants (AAPs), have used Open Burning/Open Detonation (OB/OD) for a long time as a safe and economic means to dispose of propellants, explosives, and munitions. DOD installations are required to comply with the Resource Conservation and Recovery Act (RCRA) to operate OB/OD facilities. RCRA permits provide annual limits on the amount of energetic materials that can be disposed of at OB/OD facilities. The permit limitations are based on human health risk assessments that include risk estimates from airborne exposure to pollutants generated from OB/OD. These assessments use emission factors developed mostly from a limited number of tests on small scale OB/OD chambers, known as the "BangBox", and large scale open range detonation and burn tests. There is continued need, however, to further develop methods of sampling these events to add to, and support, current data.

1.2 Objectives

This project has two objectives, both method development and measurement of source emission factors. These will be pursued through development and testing of the "Flyer" as a measurement and sample collection device with field application to measurement of emission factors from OB/OD.

1.2.1 Method Development for the Flyer

The Flyer is a lightweight platform that is intended to support sampling, CEM, and data logging capabilities while being lofted by a tethered balloon within the downwind plume evolving from some burn or detonation event. Figure 1-1 illustrates the Flyer in an initial configuration. As presented in this figure, it is configured

with battery, pumps, non-dispersive infrared (NDIR) carbon dioxide CEM, PM sampling by filter, polyurethane foam (PUF) cartridge for semi-volatile organics, and a data logger for CO₂, flow, and temperature data. Figure 1-2 illustrates the Flyer in operation, lofted by a tethered balloon. The two all-terrain vehicles (ATVs) with tether connections permit controlled positioning of the flyer within the plume. Global positioning system (GPS) measurements will be used to determine the position of the Flyer (altitude, coordinates) relative to the OB/OD event.

1.2.2 Measurement of Emission Factors

For the purposes of the planned measurements under this project, the Flyer will be configured with a carbon dioxide CEM; Summa canister for VOCs, PUF/XAD-2 resin/PUF sampler for semi-volatile organics, and filter for particulate matter and metals determination. A small GPS will be mounted on the Flyer for monitoring its location. Additionally, sophisticated electronics using the CO₂ signal will be used to "trigger" sampling events by opening sampling valves and initiating sampling pumps. The ratio of the selected target analyte pollutants to that of the CO₂ will determine emissions factors based on carbon. With knowledge of the C composition in the ordnance and the assumption of complete C oxidation, a pollutant emission factor per mass of the original ordnance can be determined.

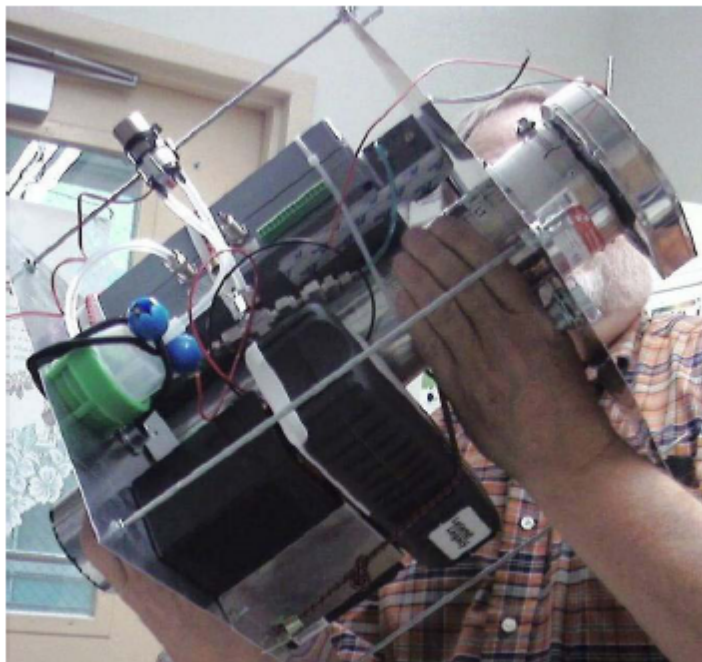


Figure 1-1. Flyer, Version 1



Figure 1-2. Lofted Flyer with ATV Positioning

1.3 Project Schedule

1.3.1 In-House Flyer Test Development and Target Compound Detection Limits

Trial runs will be performed at the EPA (RTP) facility to test the "Flyer" operability and determination of the target compounds detection limits. Two preliminary tests will be performed in RTP to satisfy these needs prior to the initiation of the field sampling campaign. These will consist of a burn hut test in January (preliminary schedule) in which the Flyer will be suspended and operated in the enclosed burn hut during a combustion test. The primary purpose of this test is to examine the hardware functioning such as the concentration-triggered sampling valves. The second test will consist of an actual sampling event with the Flyer lofted in the plume from a forest fire or sampling ambient air mimicking the actual OB/OD test. This

test will examine any hardware modifications resulting from the burn hut test and collect samples that will be used to examine detection limits. None of these data are intended for publication.

Preliminary tests are being done on sorbent contamination levels, ambient air levels of target analytes from proposed sampling media, and breakthrough tests. This will also include spike testing of Summa canisters.

1.3.2 Field Measurements

The balloon-lofted Flyer will be used to collect data and samples during the open burn (OB) and open detonation (OD) of military ordnance at the Tooele Army Depot, Tooele County, Utah in March of 2010. Figure 1-3 provides a map of the area.

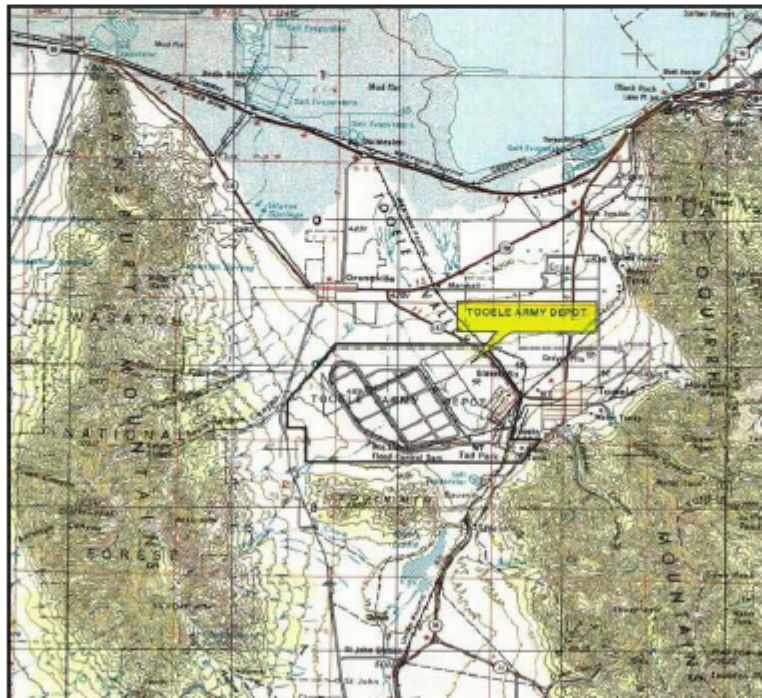


Figure 1-3. Map Locating Tooele Army Depot

Figure 1-4, supplied by Tooele Army Depot, provides a close-up map of the Test Range which consists of an indoor facility (#1376), bunkers, a gravel/sand detonation test range (~100x50 meter, small gray

rectangle), and a concrete burn pad (~20 x ~25 m, inside the small red and green circles) for open burning tests. The Army determined several initial safety stand-off scenarios as a function of charge size and plotted these on Figure 1-4. The OB and the OD tests are video monitored and recorded from the indoor facility/bunker (#1376) on Figure 1-4. The green solid line broken by green "x"s is a fence in which five gates will be installed for repositioning instruments. The elevation at the Tooele test range is about 5500 feet above sea level.

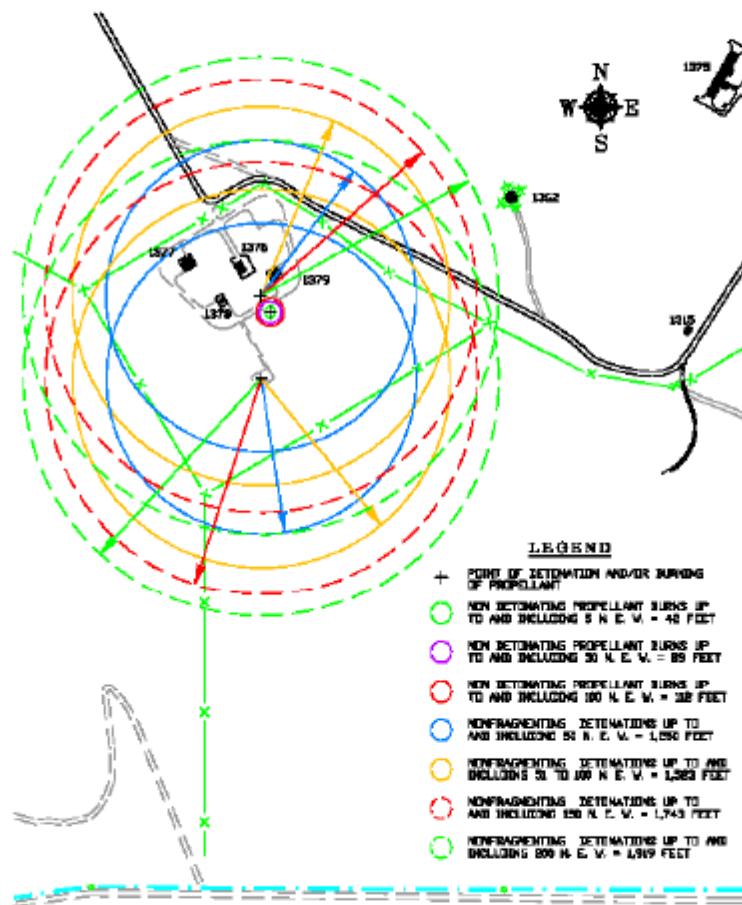


Figure 1-4. Tooele Test Facility Map

In order to predict instrument locations for optimal sampling, meteorological data such as wind speed, wind direction, and temperature will be collected from the Salt Lake City National Weather Service,

www.noaa.gov, and www.accuweather.com, which gives an hourly forecast. Additional ground level data on wind speed, wind direction, cloud cover percentage, ceiling, precipitation percentage, thunderstorm percentage, clearing index, visibility, and winds aloft will also be collected from two meteorological stations located at the Army Depot. These data are available on a daily basis from Brian Wakefield, TEAD Ammunition Production Controller, brian.j.wakefield@us.army.mil, DSN 790-5134, Commercial 435-833-2621. The weather forecast and the actual weather conditions have been shown to be in good agreement. The wind direction is mostly stable in the mornings and in the afternoons while during midday the winds are unstable i.e., fast changes in the wind direction. The predominant wind direction in the morning is from the south-southwest and shifts to the north-northwest in the afternoon. During the month of March the temperature is between 20 to 60 °F (-6 to 16°C). The Army Depot local wind data will be used to calculate the sampling module positioning in addition to personnel safety. The maximum allowed wind speed for performing the detonations and burns are 15 MPH (6.7 m/s) with gusts up to 25 MPH (11 m/s). In addition, the minimum visibilities for detonations are 1 mile with not less than 2,000 ft of ceiling (cloud cover) for detonations.

The proposed test matrix and schedule in this program are subject to changes in time and scope by the EPA WA Manager due to budget constraints or facility approval. Table 1-1 details the proposed schedule for this project.

Table 1-1. Test Schedule

Task	Start Date	Planned Completion
QAPP	December 20, 2009	January 15, 2010
In-House Flyer Test Development and Target Compounds Detection Limits	January 15, 2010	February 26, 2010
Tooele Sampling Campaign	March 8, 2010 (site preparation) and March 15 (actual sampling)	March 26, 2010
Data Analysis and Reporting		Upon Availability of the data

2. Project Organization

The organizational chart for this project is shown in Figure 2-1. The roles and responsibilities of the project personnel are discussed in the following paragraphs. In addition, contact information is also provided.

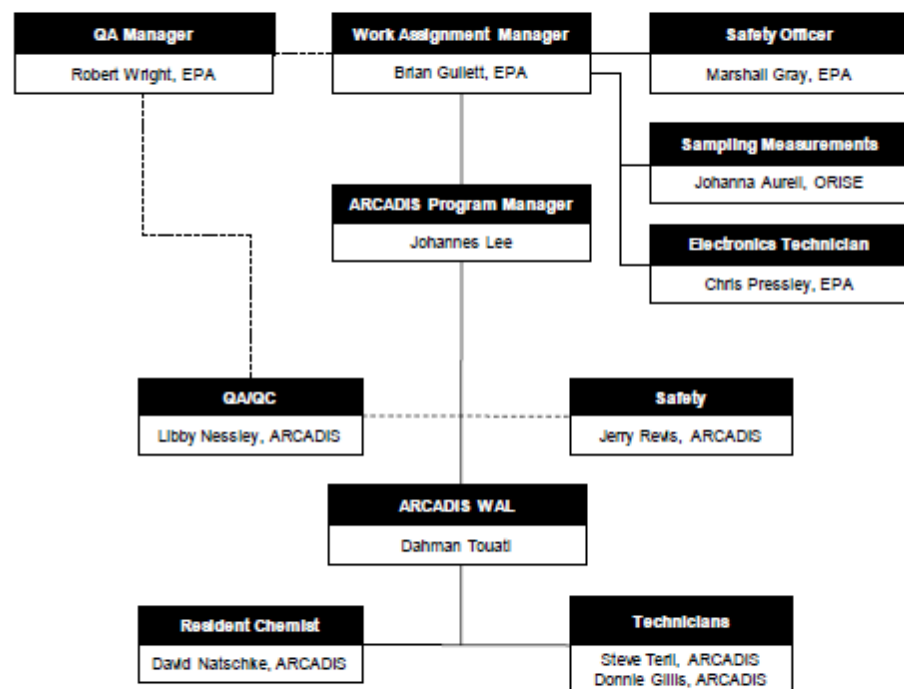


Figure 2-1. Organization Chart

EPA WA Manager (WAM), Dr. Brian Gullett: Dr. Gullett has overall project responsibility. He will direct the project's technical aspects and will be responsible for maintaining project budgets. Dr. Gullett will coordinate with EPA Quality Assurance (QA), EPA management, and with the ARCADIS WA Leader (WAL). He will schedule meetings with the ARCADIS WAL to discuss issues related to the work assignment and the necessary corrective actions to be taken. He has the authority to request a stop work order be placed on the work assignment by the Contract Officer for safety or quality control reasons.

Phone: 919.541.1534

E-mail: gullett.brian@epa.gov

EPA QA Representative, Robert Wright: The EPA QA Representative will be responsible for reviewing and approving this QAPP. In addition, this project is subject to audits by EPA QA. Mr. Wright is responsible for coordinating any EPA audits.

Phone: 919.541.5510

E-mail: wright.robert@epa.gov

EPA Electronics Technician, Chris Pressley: Mr. Pressley will be responsible for Flyer instrument wiring and connections, and data logging.

Phone: 919.541.1363

E-mail: pressley.chris@epa.gov

Post-doctoral Fellow of National Research Council, Dr. Johanna Aurell: Dr. Aurell will be helping Dr. Gullett for all the technical aspects of the projects, including the design of the test matrix, participation in the sampling campaign, and data reporting at the discretion of the EPA WAM. Dr. Aurell will be responsible for sampling and data collection.

Phone: 919.541.5355

E-mail: Aurell.Johanna@epa.gov

EPA Organic Laboratory Manager, Dennis Tabor: Mr. Tabor will be responsible for the analytical work associated with the project. Mr. Tabor will review any samples sent to an outside laboratory for data quality measures and review subsequent laboratory analytical reports.

Phone: 919.541.2686

E-mail: Tabor.dennis@epa.gov

ARCADIS WAL, Dr. Dahman Touati: The ARCADIS WAL is responsible for preparing project deliverables and managing the WA. He will assist in analytical data reduction, validation, and reporting. He will ensure the project meets scheduled milestones and stays within the budgetary constraints agreed upon by EPA. The WAL is responsible for communicating any delays in scheduling or changes in cost to the EPA WA Manager as soon as possible.

Phone: 919.541.3662

E-mail: dtouati@arcadis-us.com

ARCADIS QA Officer, Laura Nessley: The ARCADIS QA Officer is responsible for reviewing and approving any data analyses conducted by ARCADIS. Any report prepared for EPA will be reviewed by Ms. Nessley and at least 10% of the calculations will be verified with the raw data sheets, notebooks, etc.

Phone: 919.328.5588



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E-mail: lnessely@arcadis-us.com

ARCADIS Safety Officer, Jerry Revis: Mr. Revis will be responsible for ensuring that this project is carried out in accordance with all permit and EPA safety requirements. He will also ensure that anyone working on the project has fulfilled all of the safety training requirements.

Phone: 919.328.5573

E-mail: jrevis@arcadis-us.com

ARCADIS, David F. Natschke: Mr. Natschke is an ARCADIS senior chemist. He is responsible for the drafting and finalization of this quality assurance project plan. As directed by the WAL, he may perform other duties under this work assignment.

Phone: (919) 541-2347

E-mail: dnatschke@arcadis-us.com

A team of ARCADIS technicians will assist the WAL with operation, sampling, and maintenance of facility equipment used on this project.

ARCADIS, Donnie Gillis: Mr. Gillis and Mr. Terll will be responsible for assisting in the Flyer maneuvering for sample collection and will assist the WAL in all aspects of the project.

Phone: (919) 541-1066

E-mail: dgillis@arcadis-us.com

ARCADIS, Steve Terll: Mr. Terll and Mr. Gillis will be responsible for assisting in the Flyer maneuvering for sample collection and will assist the WAL in all aspects of the project.

Phone: (919) 541-4315

E-mail: sterll@arcadis-us.com

3. Experimental Approach

3.1 Sampling Approach

The purpose of the planned Tooele Army Depot sampling is to demonstrate the Flyer sampling technology for determination of emission factors from OB/OD of military ordnance. This will be accomplished by collecting plume samples to calculate concentration data for selected analytes. A limited set of target analytes, selected from those for which emission factors exist and for which there is a reasonable degree of confidence, is sufficient to satisfy the technology demonstration purposes of this project. The target analytes for this project will be benzene, naphthalene, lead, and total particulate matter. These analytes represent a range of anticipated OB/OD products and, hence, represent a broad range of sampling methods/equipment. The VOC, semi-volatile, and filter samples will be analyzed to calculate concentrations for these analytes. The CO₂ CEM data will be used to calculate a co-sampled carbon concentration, which will permit conversion of analyte concentrations to emission factors by a carbon balance method. In this method, the ratio of the sampled target analyte concentration to the total sampled carbon (as CO₂) is related back to the initial ordnance weight through knowledge of the carbon concentration in the original ordnance and the assumption of 100% oxidation of the carbon.

The Flyer, Figure 1-1, is a loftable, instrument-bearing platform for the collection of batch gas and particle samples from ambient air or plumes, the collection of CO₂ via continuous emission monitors, and the logging of data. It includes programmable logic control hardware that may, for example, enable sampling only when CEM data indicates that the Flyer is located within a plume. Power for the instruments is provided by replaceable, rechargeable battery sources. Previous work has shown that the mass of the Flyer (ca. 10 kg) is within the lofting capabilities (~15 kg at sea level) of the Kingfisher (K13N) 13×10.3 foot-diameter helium balloon, Figure 1-2. The balloon is tethered using Spectra line to a pair of ATVs equipped with electrically powered winches. The combination of two ATVs and two tethers permit the positioning of the balloon, and therefore the Flyer, at a specific location and height downwind of a source. Calculations from wind direction and speed permit calculation of the target location and elevation. A third potential tether and winch will be used to provide a third, vertical dimension for the Flyer below the balloon, if necessary.

As described in section 1.2.1, the Flyer is being configured for this project with a carbon dioxide CEM, VOC sampler with a Summa canister, semi-volatile sampling with a sandwiched PUF/XAD-2/PUF sampler, particulate sampling by filter, and temperature plus relative humidity using a HOBO (U12-013) sensor with data logging. CEM data are logged to an on-board HOBO U12-006 unit.

During the March sampling campaign, samples will be collected from both OB and OD of M1 propellant and trinitrotoluene (TNT), respectively. Table 3-1 provides the composition of these materials, while Table 3-2 provides available emission factors for the target analytes.

Table 3-1. Composition of OB and OD Ordnance

Material	Mass %	Composition	
M1	84	Nitrocellulose	$C_6H_7(NO_2)_3O_5$
	9	2,4-dinitrotoluen (DNT)	$C_6H_3(CH_3)(NO_2)_2$
	5	Dibutyl phthalate (plasticizer)	$C_{16}H_{22}O_4$
	1	Diphenylamine	$(C_6H_5)_2NH$
	1	Lead carbonate	$PbCO_3$
TNT	100	Trinitrotoluene	$C_7H_5N_3O_6$

Table 3-2. Emission Factors

Analyte	Units	TNT, OD	M1 propellant, OB
CO ₂	lb/lb C	3.5	3.6
Naphthalene	lb/lb NEW	$1.3 \cdot 10^{-6}$	$1.9 \cdot 10^{-8}$
Pb	lb/lb NEW	NA	0.0078^{\dagger}
PM ₁₀	lb/lb NEW	7.2	0.0069
Benzene	lb/lb C	$2.6 \cdot 10^{-4}$	$1.4 \cdot 10^{-5}$

lb/lb C pound per pound carbon

lb/lb NEW pound per pound net explosive weight

NA not available

[†] Calculated from Table 3-1 composition data assuming 100% release

Source: AP-42 (2009).

Sampling will occur after each of single or multiple (in series) open burns and open detonations. Multiple burns or detonations may be necessary in order sample enough of the target analytes to exceed method detection limits or background levels while keeping the charge size sufficiently small that our safety stand-off distance doesn't preclude adequate concentrations. This single, composite sample will be created by reusing the same sorbent media during multiple burns or detonations. The number of burns or detonations necessary to obtain sufficient sample will be determined by pre-test, CO₂-only measurement trials during the week of March 8th designed to understand what level of pollutants can be anticipated and at what rate from a single OB and single OD trial test. The CO₂ concentration will be used as a surrogate measure of the plume's pollutant concentration. For some target analytes (e.g., naphthalene), it is likely that multiple burns or detonations in series will be necessary in order to create a single sample that exceeds detection limits. It is almost certain that OD will be sampled after serial detonations in order to achieve higher pollutant concentrations; OB is less certain to be in series as sufficient concentrations for all target analytes may be observed during single burn tests.

For each of the OB and OD scenarios, a five day sampling campaign, with morning and afternoon test series, is planned. For the first week, five days of morning and afternoon tests will result in nine OB series (the first day will include background sampling and one test series) each of which may include multiple test burns. Similarly, the second week will result in five days of morning and afternoon OD series for a total of nine series. For each critical analyte, five replicate samples will be the project goal, although more are desirable. Each target analyte is measured by a different instrument that can be moved on or off the Flyer as needed. The number of analytes that can be sampled simultaneously will be determined by instrument weight restrictions, battery life considerations, and Flyer performance. Hence, the maximum number of tests that a single analyte will be sampled is nine for OB and nine for OD, plus background and blank samples. The minimum desirable tests for a single analyte is five for OB and five for OD, plus background and blank samples.

3.2 Analytes and Process Measurements

The following list describes the critical measurements:

Benzene
Naphthalene
Carbon dioxide
Total solid particulate
Lead
Sampling flow rates

Table 3-3 presents the planned sampling and analysis methods

Table 3-3. Sampling and Analysis Methods

Target Compound	Sampling Method	Sampling Rate	Analysis
Benzene	TO-15 Summa	0.6-3 L/min	GC/LRMS
Naphthalene	TO-15, Summa	0.6-3 L/min	GC/LRMS
Naphthalene	Modified TO-13, PUF/XAD-2/PUF	250 L/min.	GC/LRMS
PM	Filter	15 L/min	Analytical Balance
Lead	Filter	15 L/min	Compendium Method IO-3.3, EDXRF
Carbon dioxide	CEM	Every second	NDIR CEM
Carbon dioxide	EPA Method 25C, Summa	0.6-3 L/min	GC
Temperature	Thermistor, variable resistor	Every second	HOB0 U12-013
Relative humidity	Electronic sensor	Every second	HOB0 U12-013
Flowrate	Differential pressure venture	Every second	HOB0 U12-013

3.3 Test Specific Sampling Procedures

3.3.1 Open Burning

The balloon and Flyer will be prepositioned downwind of the burn site with the aid of small release balloons and smoke grenades. Two ATVs with electric winches and tethers will be used to anchor and maneuver the balloon. The ATVs and the balloon, as well as all personnel, will be located outside the safety stand-off distance. Each ATV will have a driver. If a vertical tether is used, the third tether will also have an attendant. The M1 propellant will be ignited and the ATVs will be adjusted to maneuver the balloon into the plume, guided by binocular-aided visual observation and a high visibility light which is activated by a CO₂ level trigger.

Optimal locations for plume collection will be calculated prior to the event using the Open Burn Open Detonation Model (OBODM) computer model (Cramer, 1998) and local meteorological conditions. During the week of March 8th, an initial, single, "pre-sampling" M1 burn will be used to verify the model output and to determine effective burn duration and the CO₂ concentration-time profile. This sampling may alternatively use a smaller Kingfisher balloon which has a rated lift of 8 lbs. The larger balloon was tested and found to have a practical lift of 43 lbs versus its rated lift of 34 lbs. When accounting for a 3%/1000 ft altitude penalty, we anticipate a 6.8 lb practical lift for the small Kingfisher which will enable us to easily loft the 2.2 lb LI-COR Biosciences LI-820 CO₂ monitor and its 2 lb pump/filter and battery. This pre-sampling burn will determine the frequency of burn ignitions and the optimal standoff distance. If the elevated CO₂ profile is short in time, then the period between the serial ignitions should be short. If the profile is sustained, then a longer period is sufficient. These profile data also need to be reconciled with required standoff distances and optimal post-ignition positioning. If sufficient concentrations are possible outside of the safety arc, then successive ignitions will not require personnel retreat beyond the safety arc. Successful plume location and pollutant concentrations will be determined by examination of the HOBO data of logged CO₂ concentration and analysis of the CO₂ and benzene (during the actual testing) concentrations in the Summa canisters. These canisters will be sent via overnight courier to an analytical laboratory in California (CasLab, Simi Valley) for analysis. CasLab was selected after talking to three vendors on the basis of their very low naphthalene detection limits, their ability to run low level calibration curves for naphthalene, and their ability to respond quickly. These data will provide feedback on our ability to successfully maneuver into the plume and our mass collection rate of pollutants, complementing our CO₂ data. On-board GPS measurements will be used to determine the position of the Flyer (altitude, coordinates) relative to the OB/OD event and, with CO₂ measurements, be used to determine the efficacy of the OBODM output.

The likely testing scenario will include successive burns, timed to insure high concentrations within the plume, but with enough time to maneuver the Flyer for optimal plume capture. Up to eight burns in series with a charge of 100 lb each of M1 propellant per burn are envisioned for each event, for a total of 1600 lbs per day (morning and afternoon series) maximum (see Table 3-4). The M1 will be burned on a concrete pad

(Figure 3-1) with a metal burn pan. At the time of this writing, re-usable, sheet steel pans were being constructed with a 100 lb capacity, although two co-located pans might be ignited simultaneously to achieve a 200 lb burn, if desired (see Figure 3-2). Each burn will have about 5-10 minutes between burn ignitions, depending on the plume duration. The estimated sampling time is up to 10 minutes per burn. To the extent possible, the burn pans will be aligned collinearly with the burn vector to minimize Flyer repositioning. The number of ignitions will depend on the calculated amount necessary to exceed the analyte detection limit, judged from historical emission factors and the rate and amount of CO₂ collected at the site during the pre-sampling trial burn. Upon detection of sufficiently elevated carbon dioxide levels above background, determined in part by the single pre-test and small balloon CO₂ measurements, a trigger circuit will initiate VOC and semi-volatile sampling.

Sampling time estimates for each target analyte used literature emission factors, ambient air background concentrations, and our preliminary analyses of the contaminant level of the sampling media. The most difficult analytes to detect are likely naphthalene and benzene. Published emission factor values were used in OBODM to predict plume concentrations. Together with our method sampling rates, required analyte mass was determined. These mass values were then compared to the ambient air levels and method detection limits. The estimated sampling times necessary to equal or exceed ambient air levels and/or method detection limits were determined and presented in Table 3-5. This values should only be construed as an order of magnitude approximation due to compounding uncertainty in emission factors and in the OBODM dispersion model.

It is anticipated that personnel will always be outside of the safety range during ignition and burning. Upon completion of the event sampling (one to four burns), the Flyer will be brought down. Data will be downloaded from the on-board data logger. The Summa canister will be removed, sealed, and shipped to the laboratory with its chain of custody sheet (COC, see section 3.9). The semi-volatile sampling media sandwich will be removed, logged, and preserved before shipment to RTP. The filter sample will be logged and its COC will be shipped to an outside laboratory for Pb analysis by EDXRF and total PM by gravimetric analysis.

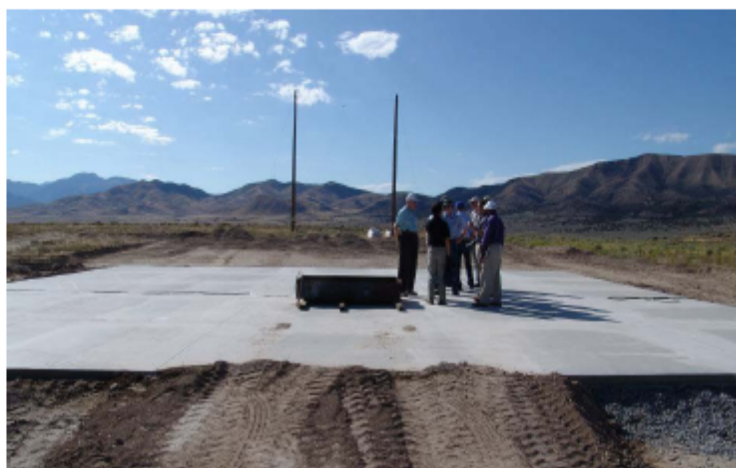


Figure 3-1. Open Burn Site

Table 3-4. Open Burn Test Plan

Date	M1 burn	VOC, Summa canister	Semi-volatiles, PUF/XAD-2/PUF	Pb and PM	CO ₂
3/15/2010		Field blank	Field blank	Field blank	Background (upwind)
		Background (upwind)	Background (upwind)	Background (upwind)	Background (upwind)
	8*100 lb	X	X	X	X
3/16/2010	8*100 lb	X	X	X	X
	8*100 lb	X	X	X	X
3/17/2010	8*100 lb	X	X	X	X
	8*100 lb	X	X	X	X
3/18/2010	8*100 lb	X	X	X	X
	8*100 lb	X	X	X	X
3/19/2010	8*100 lb	X	X	X	X
	8*100 lb	X	X	X	X
3/20- 21/2010	spares				

Total of 7200 lbs M1; X = Analyte sampling. Number of analytes sampled during each run will be determined by on-site-determined concentrations and sampling times.

Table 3-5. Required sampling time from multiple burns to surpass anticipated ambient background (PM is considered non-consequential)

Target Compound: sampling method	ΔTime-average concentration in the plume (2 min, μg/m ³)	ΔTime- average concentration in the plume (6 min, μg/m ³)	Ambient air conc. (μg/m ³)	XAD conc. (μg/sample)	Required sampling time (min) ⁻¹ within the first...	
					2 min of the burn	6 min of the burn
Benzene: Summa canister	0.87	0.29	0.55	NA	2	NA
Naphthalene: Summa canister	0.02	0.005	0.006	NA	2	NA
Naphthalene: PUF/XAD-2/PUF	0.02	0.005	0.006	0.02	4	NA
Lead: filter	TBD	TBD	0	TNA	TBD	TBD

CO ₂ :	NDIR CEM	222 ppm	74 ppm	~ 390 ppm	NA	NA	NA
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*1. The sampling time range for sampling with summa canister is dependent on the sampling flow rate, 0.0006-0.003 m³/min; TBD – to be determined



Figure 3-2. Open Burn Pan (TNT flakes shown)

Due to naphthalene's vapor pressure (1.1×10^{-2} kPa) and boiling point (218 °C) it can show both volatile (VOC) and semi-volatile (SVOC) characteristics. According to EPA Method TO-13 [1] using only filter media prevents efficient collection of certain volatile PAH (naphthalene), and "particulate-phase PAHs will tend to be lost from the particle filter during sampling due to volatilization". In addition, the method also state that naphthalene has only ~35% recovery using PUF as the sorbent media and it is recommended to use XAD-2 resin as the sorbent media when sampling for naphthalene. The method also states that PAH "with vapor pressures above approximately 10⁻⁸ kPa will be present in the ambient air substantially distributed between the gas and particulate phases".

The ambient air concentrations at Tooele from NATA 2002 (0.006 ug/m³) is modeled. The naphthalene concentrations were modeled using the emissions-based methodology using emission inventory data [2]. Based on what Method TO-13 states and due to naphthalene's characteristics it should not be present in the atmosphere in particulate form. The data from the emission inventory and monitored data should be sampled according to methods, hence the NATA value should not be multiplied by 4 (i.e. 0.006 ug/m³ already represents both gas and particulate phase).

A better knowledge of the actual naphthalene and benzene background concentrations at Tooele will be available the second week of sampling since background samples will be sampled and shipped for analyses during the first week.

The Tooele naphthalene background concentration is cited as $0.006 \mu\text{g}/\text{m}^3$ (NATA, 2002). Based on literature values for emission factors (Table 3-2), OBODM was used to estimate the plume concentration at the Flyer under anticipated sampling conditions (100 lb of M1, 35 m from the burn, height of 15-20 m, and a wind speed of 2 m/s). Since the literature-cited emission factor for naphthalene (Table 3-2) was determined by sampling semi-volatiles on a quartz-fiber filter (DTB, 1992), it only reflects the particulate phase and misses the volatile phase. A recent ambient air study (He & Balasubramanian, 2009) showed that 20% of the ambient air concentration of naphthalene is found in the particulate phase. Hence, the OBODM-predicted plume concentration was increased by 4X to about $0.02 \mu\text{g}/\text{m}^3$ as a more accurate prediction of the time-averaged plume concentration from 0 to 2 min (the minimal OB plume sampling time that we reasonably anticipate we can sample). Our preliminary tests for the PUF/XAD method have shown that the naphthalene sampling media, XAD-2, is contaminated with naphthalene even after cleanup, confounding distinctions with sampled emissions. However we have been able to reduce the media concentration from 15 ng naphthalene/g XAD-2 to 1 ng naphthalene/g XAD-2, meaning that each field sample would have a contaminant concentration of 0.02 μg on the 20 g of XAD-2. To obtain an equal amount of naphthalene from the M1 burn as from the XAD contamination we need to sample for 4 and 3 minutes for 100 and 200 lb charges, respectively, at the OBODM-predicted 2 min time-average concentration, or about three burns. We also believe that more than 2 min of effective sampling can be done on each open burn. The PUF/XAD method will also be complemented by the Summa canister method which may show greater ease of detection.

Use of the emission factor for benzene (Table 3-2) in OBODM shows that the plume concentration easily exceeds the ambient air level of $0.55 \mu\text{g}/\text{m}^3$ (NATA, 2002). The ratio of sampled emissions and background emissions would be 2/1 for benzene when sampling from 0 to 2 min after ignition. Hence, benzene poses less of a sampling time (volume) challenge than naphthalene.

3.3.2 Open Detonation

The balloon and Flyer will be pre-positioned downwind of the detonation site with the aid of small balloons

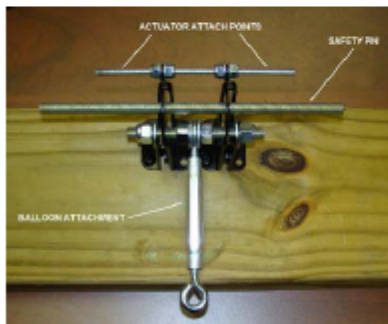


Figure 3.3. Balloon release mechanism.

and smoke grenades. Two ATVs with electric, remotely-controlled winches and tethers will be used to anchor and maneuver the balloon. The ATVs and the ground-fixed balloon/Flyer will likely be located inside the safety stand-off distance, each behind shrapnel/rock-protective bunkers. All personnel will be outside of the stand-off distance and behind a protective bunker. When the balloon is no longer in danger of being damaged from the shrapnel and shock wave of the last detonation, it will be released to fly up into

position. The balloon/Flyer will be released from its ground-based shelter using wireless (2.4GHz) remote control to open the balloon clamp (see Figure 3-3). The clamp will be opened by using two 12VDC powered linear actuators with a two inch throw. Each actuator will provide 18lbs of pull force that will be more than sufficient to actuate the release. The release mechanism will have provisions for a safety pin to prevent inadvertent release during setup and configuration. This release mechanism, its battery, radio receiver, and ballast will be mounted on a pallet. The pallet will have enough ballast to safely endure the detonation shock wave and any gusts of wind that may occur prior to release. Once deployed, the balloon will be maneuvered by retracting and extending the electric winches via remote control. Additional maneuvering can be achieved by manning the ATVs with drivers but this will only be done after the required safety period for personnel has expired and/or permission has been given by the range control officer. To keep the balloon/Flyer's location optimized in the plume, personnel will use visual observation and a high-CO₂ – triggered flashing light mounted on the Flyer.

An initial, single, "pre-sampling" detonation during the week of March 8th will be used to determine effective shrapnel zones (for the equipment), plume duration, and the CO₂ concentration-time profile. This detonation will determine the frequency of detonations and the optimal standoff distance. If the CO₂ profile is short in time, then the period between ignitions should be short. If the profile is sustained, then a longer period is sufficient. Modeling, however, predicts rapid dispersion of the pollutants, requiring detonations in rapid succession. This will ensure high concentrations within the plume, but with enough time to maneuver the Flyer for optimal plume capture. This may mean about 5-15 seconds between detonations. The number of ignitions will depend on the calculated amount necessary to exceed the analyte detection limit, judged from historical emission factors and the rate and amount of CO₂ collected at the site.

On each morning or afternoon of sampling, up to three detonations in series with a charge of 100 lb each of TNT will occur, for a total of 1,200 lbs per day, maximum. Each detonation will have about 5-15 seconds between initiation to maximize the plume concentration while minimizing the safety standoff distance (through minimizing the charge size).

Multiple morning and afternoon detonations may be used to create a single, composite sample. This single sample will be created by reusing the same sorbent media during multiple events. The primary indicator of required composite samples will be the CO₂ mass collected and the published emission factors. Upon completion of sampling, the Flyer will be brought down for downloading the on-board data logger. The Summa canister will be removed, sealed, and shipped to the laboratory with its chain of custody sheet (COC). The Semi-volatile sampling media sandwich will be removed, logged and preserved before shipment to RTP. The pre-weighed sample filter will be logged and its COC will be shipped to a commercial laboratory for determination of PM mass and lead.

Table 3-6 presents a test plan for the open detonation tests.

Table 3-6. Test Plan for Open Detonation Sampling

Date	TNT	VOC, Summa canister	Semi-volatiles, PUF/XAD-2/PUF	PM	CO2
3/22/2010		Field blank	Field blank	Field blank	Background (upwind)
		Background (upwind)	Background (upwind)	Background (upwind)	Background (upwind)
	4*100 lb	X	X	X	X
3/23/2010	4*100 lb	X	X	X	X
	4*100 lb	X	X	X	X
3/24/2010	4*100 lb	X	X	X	X
	4*100 lb	X	X	X	X
3/25/2010	4*100 lb	X	X	X	X
	4*100 lb	X	X	X	X
3/26/2010	4*100 lb	X	X	X	X
	4*100 lb	X	X	X	X
3/27/2010	spare				

3600 lbs TNT total (5400 lbs TNT total if the site allows 3*200 lbs). Four detonations in series is limited by the current pad size. Period is 5 to 15 s between detonations with 15 s preferable by the Range personnel. Each detonation is 52 ft apart (65 ft, if 200 lbs) and the 200 lb TNT safety distance is 1,919 ft (100 lb is 1,743 ft). Charges will be placed collinearly with the wind vector, to the extent predictable.

As with OB, sampling time estimates for each target analyte used literature emission factors and ambient air background concentrations as well as our preliminary analyses of the contaminant level of the sampling media. Table 3-7 shows that only the PUF/XAD/PUF method for naphthalene may require multiple 100 lb detonations to reach desired concentration levels. At the time of writing this QA Plan, the Depot was inquiring into the possibility of detonating 200 lbs per test. Note that the literature emission factor for naphthalene is ~ 100 times higher for OD than for OB, even though the CO₂ emission factors are nearly the same.

Table 3-7. Required sampling time to surpass anticipated ambient background concentrations and method detection levels during OD. 200 lb of TNT (one charge), 61-100 m from the detonation, and wind speed of 2 m/s. (PM is considered non-consequential).

Target compound: Sampling Method	ΔTime-average concentration in the plume (2 min, μg/m ³)	ΔTime-average concentration in the plume (4 min, μg/m ³)	Ambient air conc. (μg/m ³)	XAD conc. (μg/sample)	Required sampling time (min) within the first...	
					2 min of the detonation	4 min of the detonation

Benzene: Summa canister	2.8-1.4	1.4-0.7	0.55	NA	1	1
Naphthalene: Summa canister	0.2-0.1	0.1-0.05	0.006	NA	1	1
Naphthalene: PUF/XAD-2/PUF	0.2-0.1	0.1-0.05	0.006	0.02	1	1
CO ₂ : NDIR CEM	21-10 ppm	11-5 ppm	~ 390 ppm	NA	NA	NA

3.4 Sampling methods and other critical measurements

3.4.1 Carbon Dioxide by NDIR CEM

Carbon dioxide measurements will be performed using LI-COR Biosciences LI-820 non-dispersive infrared (NDIR)-based CEMs mounted on the Flyer. This unit is configured with the optional 14 cm optical bench, giving it an analytical range of 0-2,000 ppm with an accuracy specification of <2.5% of reading. Carbon dioxide measurements are expected to vary between ~380-750 ppm. Signal averaging can be adjusted from 0-20 seconds per reading. The LI-COR Biosciences LI-820 CEM is equipped with a programmable alarm output. This output is capable of controlling solenoids as well as visual and audible alarms. Based upon preliminary tests (prior to March 15, 2010) this alarm circuit will be programmed to turn on when above ambient levels of carbon dioxide, i.e., the Flyer is within the plume. This alarm circuit will be used to turn on pumps and open solenoid valves, as described below in section 4.2. The LI-COR LI-820 is equipped with adjustable high and low alarm values and for each of these a "dead band" value can be chosen i.e., the upper alarm is activated at the chosen value and remains activated until the CO₂ concentration drops below the set dead band value.

3.4.2 Summa Canister Sampling for VOCs and Carbon Dioxide

Volatile organics will be sampled via Method TO-15 "Determination of Volatile Organic Compounds (VOCs) in Air collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)." <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf>. Sampling for VOCs will be accomplished using laboratory-supplied 6 L Summa canisters. This canister will be equipped with a pressure gauge, manual valve, critical orifice assembly (COA) and a solenoid valve, the latter controlled by the carbon dioxide trigger circuit. Columbia Analytical Services, 2655 Park Center Drive, Suite A Simi Valley, CA, 93065 will provide summa canisters with a 12V valve with orifice and filter already put together. The laboratory will configure and calibrate the critical orifice assemblies and ship them to the field along with the Summa canisters Separate valve/orifice/filter combination for an anticipated range of 1, 2, 6, and 10 minutes

are anticipated. This range of sampling durations is meant to sample the short, several minute peak concentration plumes and longer, multi-minute peak concentration plumes. The shorter sampling periods risk representativeness and the longer sampling periods risk sample dilution and detectability. These sampling rates will likely be different for OB and OD experiments, and for the number of plumes to be collected as a single sample.

The Summa canister will be hung from the bottom of the Flyer and will have its solenoid valve controlled by the LI-COR LI-820's alarm circuit. At the beginning of a sample collection, the gauge will be checked to ensure no leakage has occurred; then the manual valve will be opened. When the LI-COR LI-820 measures elevated levels of carbon dioxide, its alarm circuit will enable a solid state relay, which will open the canister's solenoid valve and sampling will occur at the critical orifice's calibrated flow rate. The solenoid valve will close and sampling will cease when carbon dioxide readings return to ambient levels. Following the end of sampling, the manual valve will be closed, the canister will be dismounted from the Flyer, the COA will be removed, and the canister will be returned to its shipping container.

Each Summa canister sample will also be used for analysis of carbon dioxide by GC, utilizing EPA method 25C. Method 25C also specifies gas sample collection by evacuated cylinder.

3.4.3 Semi-volatile sampling

In a similar manner, semi-volatile sampling will occur using a PUF/XAD-2 resin/PUF sorbent sandwich. This sandwich will be delivered to the site already mounted in a glass tube with clamping flange. The sandwich will be prepared for sampling by removing it from its shipping container, removing the aluminum foil ends, and mounting it on to a MINijammer brushless direct current (BLDC) blower (AMETEK). Semi-volatile sampling will be performed using a BLDC low voltage blower for a nominal sampling rate of 0.25 m³/min. The blower will be controlled by the carbon dioxide alarm circuit. Flow rate will be measured by pressure differential across a calibrated venturi. A venturi consists of a carefully calculated and constructed constrictor. As used here, it will be mounted on the outlet of the semi-volatile sampler. A venturi has the property that fluid pressure through a constricted section of pipe is reduced. The fluid velocity must increase through the constriction to satisfy the equation of continuity, while its pressure must decrease due to conservation of energy. As such, a measurement of ΔP between the venturi's inlet and constricted diameter body will measure this pressure drop and that data may be used to calculate flow rate. In practice, a calibration curve is developed from ΔP and actual flow measurements. The voltage equivalent to this pressure differential will be recorded on the HOBO external event logger. The APPCD Metrology lab will perform these measurements using the venturi's matched transducer and a Roots meter. Following sampling, the sandwich will be removed from the Flyer, the ends will be sealed with clean aluminum foil, it will be returned to its shipping container, and stored at 4°C until shipped to the laboratory.

Naphthalene is being sampled by the PUF/XAD method, in addition to the Summa canister method, since the Summa method has uncertain recoveries for less volatile compounds. The PUF/XAD sorbent method will also allow us to look for other semivolatiles, including PAHs.

3.4.4 Particulate matter sampling

Particulate matter sampling will occur using a 47 mm tared Teflon filter. The filters will be shipped to the site pre-tared and mounted in sealed petri dishes. The filters will be placed in a filter holder and will be connected to the sampling pump. PM sampling will be performed via an SKC Leland Legacy Sample pump with a constant airflow of 15 L/min. The internal flow sensor measures flow directly and acts as a secondary standard to constantly maintain the set flow. The volume display is continually updated, based on corrected flow rate multiplied by sampling time. The display presents the pump serial number, pump software revision level, flow rate, volume, temperature, atmospheric pressure, time of day, run time, and pump status, i.e., hold and run as well as setup information. The pump will be controlled by the carbon dioxide alarm circuit. Following sampling, the filter holders will be disassembled and the filters will be placed in 47 mm petri dishes with twist-lock closures. A gel band will also be installed as further insurance against seals opening during preservation and shipment. The sealed petri dishes will be placed in a reclosable bag pre-loaded with desiccant.

It should be noted that detonations occur on soil surfaces and, as such, the plume includes significant soil particulate matter. This is reflected in Table 3-2 where the open detonation PM_{10} emission factor is much larger than the charge weight. One grab sample will be collected from soil at the OD site using a 20 mL scintillation vial. The vial will be sealed with a non-metallic threaded cap and stored for shipment to the laboratory.

3.4.5 Sampling Time

Sample times for the Summa canister and particulate filter are not separately recorded. Sampling time for the Summa canister, semi-volatile sorbent sandwich, and particulate filter are all based upon the same carbon dioxide switched alarm. They are, therefore, identical (up to the point where the summa canister has been filled to ambient pressure, at which point it ceases to collect sample). Sample time is, therefore, based upon the semi-volatile sampling pump where voltages from the venturi's differential pressure measurement will be recorded on the HOBO external event data logger.

3.5 List of Samples

- Summa Canisters, 6 L, with calibrated critical orifice assembly hardware
- PUF/XAD-2 resin/PUF will be prepared from cleaned PUF plus manufacturer-cleaned XAD-2 resin. They will be packed in the glass samplers and sealed with clean aluminum foil. Cleaned PUF consists

of as-received PUF that is solvent cleaned using sequential toluene and dichloromethane elution. It is dried under a flowing nitrogen stream prior to use.

- Filter, Teflon, 47 mm, tared.
- Grab samples from the OD soil particulate are collected in a 20 mL scintillation vial with non-metallic caps. Cap to be sealed with vinyl or electrical tape after sample collection. An OSHA-21 seal is wrapped lengthwise after sample collection.

3.6 Sample Preservation Requirements

- Filter samples are preserved by storage under desiccant.
- Soil grab samples are stored in a sealed glass vial.
- Samples collected on PUF/XAD-2/PUF will have the ends sealed with new aluminum foil and will be refrigerated after collection. Samples must be shipped and extracted within 14 days of sampling.
- Summa canister samples for VOC analysis must be analyzed within 14 days of collection.

3.7 Numbering Method

Each sample data sheet and sample fraction will be given an identifying code number that will designate the run number. The codes and code sequence will be explained to the field team and laboratory personnel to prevent sample mislabeling. Proper application of the code will simplify sample tracking throughout the collection, handling, analysis, and reporting processes. The sample coding to be used in this study is described in Table 3-8.

For each sample a chain of custody sheet will be generated. For a sample collected in a Summa canister, this sheet will also record the canister's associated serial number and bar code. For a particulate sample, the COC will also record the filter numbering from the laboratory performing the conditioning and taring.

Table 3-8. Sample Coding

AA-CC-DD-EE-MMDDYY-HHMM		
	Sample Code	Code definition
AA	OB	Type of test (OB = Open detonation, OD = Open detonation)
CC	FB	Test condition (FB = Field blank, PM = Plume Sample, US = Upwind Sample)
DD	FT	Sampling Media (FT = Filter, SP = Sorbent Pack, SC

		= Summa canister)
EE	01	Sample Number (01, 02, 03, etc.)
MMDDYY	031510	Date Field, month/day/year
HHMM	1523	HH = Hour, numeric 24 hour convention MM = Minute, numeric 24 hour convention

3.8 Packing and Shipping

- Summa canisters are shipped to and from the field in boxes as per CasLab instructions. The critical orifice assemblies are individually wrapped in bubble wrap and shipped with the associated canister. Summa canisters are shipped overnight for morning delivery to the contract laboratory.
- Samples collected on PUF/XAD-2/PUF are shipped overnight in insulated chests with chilled refrigerator packs.
- Sampled filters are returned to the SKC cassettes and sealed with the Omega gel bands. The cassettes are marked with the sampling information. The cassettes are stored in Zip-Lock bags with desiccant. Filter samples are shipped to the laboratory separate from bulk samples.
- Grab samples in scintillation vials are shipped to the laboratory separate from air samples.
- FedEx procedures for Summa Canisters are listed below:
 - Materials, including sampling media from CasLab & Chester Lab Net, will be shipped to:

Tooele Army Depot
Building 519
Attn: Roger Hale
Tooele, UT, 84074
 - Sampled Summa Canisters will be shipped from Tooele Army Depot to:

CasLab
2655 Park Center Drive, Ste. A
Simi Valley, CA 93065
Tel: 805 526 7161
 - 47-mm filters samples will be shipped from Tooele Army Depot to

Paul Duda
Chester LabNet

12242 SW Garden Place
Tigard, OR 97223
(503)624-2183 ext. 100
fax (503)624-2653

3.9 Chain of Custody Form

CHAIN OF CUSTODY & LABORATORY ANALYSIS REQUEST FORM

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4. MEASUREMENT AND ANALYTICAL PROTOCOLS

Critical measurements are: CO₂, Pb, Total PM, benzene, naphthalene, sample flow rates, and times. This will include background (ambient) and in-plume events.

4.1 Methods

The following sections describe the analytical methods that are planned for the determination of benzene, naphthalene, carbon dioxide, total particulate, and particulate bound lead. Sampled volumes will be calculated as the multiplicand of sample flow-rate and sampling time. These are also described below.

4.1.1 VOCs

Benzene and naphthalene will be analyzed using EPA Method TO-15 (EPA, 1999), by Columbia Analytical Services using selective ion monitoring (SIM) mode GC/MS. The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. As performed here, a 1 L aliquot is pulled from the Summa canister and analyzed.

The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of about 20-25 field samples.

An internal spiking mixture containing bromochloromethane, chlorobenzene-d₅, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air is added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

A blank canister will be analyzed daily. The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

4.1.2 Semi-volatiles

Semi-volatiles and naphthalene in particular will be sampled using EPA Method TO-13 A (EPA, 1999). Semi-volatile sorbent sandwich samples will be prepared for analysis by solvent extraction utilizing dichloromethane and then concentrated by solvent evaporation. An internal standard, d8-naphthalene, will be added. Samples will be analyzed utilizing full-scan mode at first, then SIM mode for additional sensitivity, if necessary. Laboratory and field blanks will be collected and prepared.

4.1.3 Carbon Dioxide by CEM

Carbon dioxide measurements will be performed using a Biosciences LI-820 NDIR-based CEM mounted on the Flyer. This unit is configured with the optional 14 cm optical bench, giving it an analytical range of 0-2,000 ppm with an accuracy specification of <2.5% of reading. The instrument will be preceded by a filter for particulate matter removal prior to the optical lens.

4.1.4 Integrated Carbon Dioxide Measurement

Carbon dioxide will be measured by Method 25C, in which an aliquot of the collected Summa canister sample is injected into a sample loop equipped GC/FID. While method 25C is designed for nonmethane organic compounds (NMOCs), section 11.1.3 specifically cites the elution of sample CO₂. The method specifically converts all analytes first to CO₂ and then to CH₄ to provide uniform response across all analytes including carbon dioxide.

4.1.5 Total PM by Gravimetric Analysis

Total PM will be measured gravimetrically as the difference between final and tare masses for each filter. The weighing of the filters will follow the procedures described in 40 CFR Part 50, Appendix J, 1987. The analytical balance used to weigh filters must be suitable for weighing the type and size of filters and have a readability of ±1 µg. All sample filters used shall be conditioned to 20-23 °C and 30-40 % RH for a minimum of 24 h immediately before both the pre- and post-sampling weighing. Both the pre- and post-sampling weighing should be carried out on the same analytical balance, using an effective technique to neutralize static charges on the filter. The pre-sampling (tare) weighing shall be within 30 days of the sampling period. The post-sampling conditioning and weighing shall be completed within 240 hours (10 days) after the end of the sample period.

4.1.6 Lead

The particulate matter collected on Teflon filters is also appropriate for the determination of lead. EPA Compendium Method IO-3.3 (1999) specifies the analysis by energy dispersive x-ray fluorescence spectrometry (EDXRF). This method is compatible with particulate on filters, is quite sensitive for lead, and is non-destructive. This means that the particulate matter and substrate survive the analysis intact; and may be archived or analyzed by other methods.

4.2 Calibration

4.2.1 VOCs

Prior to the analysis of samples and blanks, but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

4.2.2 Semi-volatiles

The GC/MS will be calibrated using a 5-point calibration with d8-naphthalene internal standard.

4.2.3 Carbon Dioxide by CEM

The LI-COR Biosciences LI-820 NDIR-based CEM is calibrated using a zero (nitrogen) and span gas (CO₂ in nitrogen). This will be performed in the laboratory prior to transportation to the field. Linearity checks will be performed in the lab following the calibration using two additional cal gases of intermediate CO₂ concentrations.

In the field, zero and span checks will be performed on a daily basis.

4.2.4 Integrated Carbon Dioxide

The GC is calibrated utilizing carbon dioxide in nitrogen certified calibration gases. A 4 point calibration will be performed.

4.2.5 Total PM by Gravimetric Analysis

Calibration for determining mass of conditioned media is performed as per "Quality Assurance Guidance Document 2.12".

4.2.6 Lead

In general, calibration determines each element's sensitivity, *i.e.*, its response in x-ray counts/sec to each $\mu\text{g}/\text{cm}^2$ of a standard and an interference coefficient for each element that causes interference with another one (See section 3.2 above). The sensitivity can be determined by a linear plot of count rate versus concentration ($\mu\text{g}/\text{cm}^2$) in which the slope is the instrument's sensitivity for that element. A more precise way, which requires fewer standards, is to fit sensitivity versus atomic number. Calibration is a complex task in the operation of an XRF system. Two major functions accomplished by calibration are the production of reference spectra which are used for fitting and the determination of the elemental sensitivities. Included in the reference spectra (referred to as "shapes") are background-subtracted peak shapes of the elements to be analyzed (as well as interfering elements) and spectral backgrounds. Pure element thin film standards

are used for the element peak shapes and clean filter blanks from the same lot as routine filter samples are used for the background. The analysis of Pb in PM filter deposits is based on the assumption that the thickness of the deposit is small with respect to the characteristic Pb X-ray transmission thickness. Therefore, the concentration of Pb in a sample is determined by first calibrating the spectrometer with thin film standards to determine the sensitivity factor for Pb and then analyzing the unknown samples under identical excitation conditions as used to determine the calibration. Calibration shall be performed annually or when significant repairs or changes occur (e.g., a change in fluorescence X-ray tubes, or detector). Calibration establishes the elemental sensitivity factors and the magnitude of interference or overlap coefficients.

Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter. Thin film standards are typically deposited on Nuclepore substrates. Thin film standards are available from NIST and commercial sources.

A background spectrum generated by the filter itself must be subtracted from the X-ray spectrum prior to extracting peak areas. Background spectra must be obtained for each filter lot used for sample collection. The background shape standards which are used for background fitting are created at the time of calibration. If a new lot of filters is used, new background spectra must be obtained. A minimum of 20 clean blank filters from each filter lot are kept in a sealed container and are used exclusively for background measurement and correction. The spectra acquired on individual blank filters are added together to produce a single spectrum for each of the secondary targets or fluorescers used in the analysis of lead. Individual blank filter spectra which show atypical contamination are excluded from the summed spectra. The summed spectra are fitted to the appropriate background during spectral processing. Background correction is automatically included during spectral processing of each sample.

4.2.7 Sampling Flowrate

- Summa canister sampling rate is based upon a calibrated critical orifice assembly (COA) supplied by the commercial analytical laboratory supplying the canisters. The COA will be configured as per the WAM's instructions and calibrated by the supplying laboratory.
- Semi-volatile sampling utilizes the BLDC blower. The flowrate is measured by the pressure differential measured across the installed venturi. The voltage equivalent to this pressure differential will be recorded on the HOBO™ external event logger. This will be calibrated in the APPCD Metrology laboratory prior to being deployed utilizing a Roots meter.
- The filter sampler utilizes an SKC Leland Legacy constant rate sample pump. The patented (U.S. Patent No. 5,892,160) internal flow sensor measures flow directly and acts as a secondary standard to constantly maintain the set flow. Set flow is achieved immediately at start-up and flow calibration is automatically maintained by built-in sensors that compensate for differences in temperature and atmospheric pressure during sampling. Flow rate: $\pm 5\%$ of set-point after calibration to desired flow. The

Leland Legacy is programmable with the Leland DataTrac Software using a PC and will presents the pump serial number, pump software revision level, flow rate, volume, temperature, atmospheric pressure, time of day, run time, and pump status, i.e., hold and run as well as setup information. The volume display is continually updated, based on corrected flow rate multiplied by sampling time. The pump will be calibrated with the Gilibrator Air Flow Calibration System (Scientific Instruments), which is a primary standard airflow calibrator.

4.2.8 Sampling Time

Sampling time will be based upon data logged onto the HOBO U12-006 4-channel external logger. Each recorded event is time and date stamped. The HOBO maintains an internal time, which has a time accuracy of ± 1 min per month. Since all sample times are based upon differentials across sampling times on the order of several minutes, no further calibration is necessary.

4.2.9 GPS

The GPS measurements on board the Flyer are not critical measurements but will be used in retrospect, along with the CO₂ time data, to assess the predictive capability of OBODM. The altimeter and the electronic compass in the GPS need to be calibrated before use and after every time the batteries are changed. In order to calibrate the altimeter the current elevation or barometric pressure must be known, which has to be received from a reliable source at Tooele. To receive an accurate calibration of the electronic compass the GPS needs to be leveled and not nearby magnetic fields such as cars and buildings.

5. QUALITY ASSURANCE/QUALITY CONTROL

5.1 Comparisons

As a QA check, the results obtained from integrated extractive sampling and analysis by conventional methods will be compared to the corresponding continuous sampling techniques, when available.

5.2 Quality Objectives and Criteria

The objective of this project is to characterize the emissions for OB/OD events. The data quality objectives (DQOs) define the critical measurements (CM) needed to address the objectives of the test program, and specify tolerable levels of potential errors associated with data collection as well as the limitations of the use of the data. However, the critical measurements used in the computation of the emission data shall also satisfy the data quality indicator goals specified by the respective sampling methods based on a Pass/Fail criterion, such as pre-sampling surrogates recoveries that are not included in the computation.

The following measurements are deemed to be critical to accomplish the project objectives:

- PM weights
- Target pollutant concentrations
- Sample volumes
- Sampling time

These measurements are needed to determine the emission factors and emission rates for the various pollutants. The time sequence of sampling events must be recorded on the same time axis as are the current CEM data streams. This is essential to determine the extent of the emissions as a function of the damper mode (closed or open) and the fuel charge consumption as a function of time.

5.3 Data Quality Indicator Goals for Critical Measurements

The data quality indicators (DQIs) are specific criteria used to quantify how well the collected data meet the DQOs. The DQI goals for the critical measurements correspond to and are consistent with the standards set forth in each respective referenced EPA Method. Accuracy and precision estimates are available where noted, and completeness goals for data collection and sampling are indicated in Table 5-1.

Table 5-1. Data Quality Indicators

Measurement Parameter	Analysis Method	Recovery	Detection Limit	Completeness %
Benzene	EPA Method TO-13 A	NA	0.15 µg/m ³	90
Naphthalene	EPA Method TO-15	70-130%	0.1 µg/m ³	90
Naphthalene	EPA Method TO-13 A	25-130%	30 ng/m ³	90
Carbon dioxide	GC	95%	NA	90
Measurement Parameter	Analysis Method	Accuracy	Detection Limit	Completeness %
PM	Analytical Balance	15 %	1 µg	90
Lead	EDXRF	8%	0.45 µ/m ³	90
Carbon dioxide	NDIR CEM	3 % of reading	NA	90
Flowrates	Venturi differential pressure	99+%	NA	100
	Internal flow sensor	± 5 % set point	NA	100

5.3.1 DQI Goals for the Target Pollutants

The DQI goals for the critical measurements for PM and organic sampling (listed in Table 5-1) correspond respectively to the standards set forth in each respective EPA Method.

5.3.1.1 PAHs

A single TBD deuterated PAH (see Table 5-2) will be added to the XAD-2 trap before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of the sampling train collection efficiency. All surrogate standard recoveries shall be between 25 and 130 percent. A deuterated recovery standard, TBD, will be added before mass analysis.

Table 5-2. PAH Surrogates, Composition & Purpose

Spiking Solution	Analytes	Special Notes
Pre-sampling surrogate	TBD, deuterated PAH; Naphthalene std	added to sorbent pack prior to shipment to field
PAHs - Internal Standards	Naphthalene-D8	Added to the sample prior to extraction
Recovery	TBD, deuterated PAH	Added before mass analysis

5.3.2 Representativeness and Comparability

At least five samples per analyte are targeted for measurement and comparison. Results will be compared with minimally existent emission factors from the literature.

5.4 Assessing DQI Goals

In general, data quality indicator goals are based on either (1) published specifications, (2) related quantities (like drift for precision), or (3) engineering judgment based on previous experience with similar systems.

5.4.1 Precision

In order to measure precision, it is necessary to make replicate measurements of a relatively unchanging parameter. The ability to measure precision is dependent upon the type of data that is being measured. With an analytical balance or a CO analyzer, all it takes to measure precision is to measure the value of a reference standard more than once and compare the two numbers. To check precision, any pair of duplicate measurements can be entered into an equation of the form:

$$RPD = \frac{100 \times |Q - B|}{(Q + B) / 2} \quad (5-1)$$

Where:

Q = results from one run

B = results from second duplicate run

RPD = relative percent difference

If more than one pair of duplicate measurements is available, an entire population of individual precision can be generated. The best way to represent all of the replicate responses to a reference standard is with a relative standard deviation (RSD):

$$RSD = \frac{\sqrt{\sum_{i=1}^n (Y_i - \bar{Y})^2}}{\sqrt{n-1} \bar{Y}} \quad (5-2)$$

This is often expressed as a percent.

When there are no reference standards, however, precision calculations are at the mercy of system stability. Furthermore, several of the measurements only generate one value per run (i.e., for 2 runs per condition, Precision = RPD). Therefore, for measurements that are compared to a reference standard, precision can be measured on a per-run basis as RPD. Overall precision for the entire test series can be expressed as RSD. For measurements that have no reference standard, precision is expressed as RSD for multiple measurements per run, and as RPD for singular measurements.

5.4.2 Accuracy

The accuracy of a measurement is expressed in terms of percent bias, or, in some cases recommended by the EPA standard methods, in terms of absolute difference. Percent bias is defined as:

$$\text{Percent Bias} = \frac{R - C}{C} \times 100 \quad (5-3)$$

Where: R = instrument response or reading

C = calibration standard or audit sample value

Accuracy can take on the units of the measurement, it can be expressed as a percentage of the average measurement, or it can be expressed as a percentage of the measurement range.

5.4.3 Completeness

The ratio of the number of valid data points taken that meet DQIs goals to the total number of data points planned is defined as data completeness. All measured data are recorded electronically or on data sheets or project notebooks.

6. DATA ANALYSIS

Data produced includes notes recorded in a laboratory notebook, digital photos of the filters and PUFs, data from the EPA laboratory analyses, and all the sample analysis produced by the accredited laboratory. One laboratory notebook at a time will be maintained for this project, to be used for recording data by any personnel. This laboratory notebook will be archived by the EPA WAM.

6.1 Data Reporting

For each run, digital acquisition data, pictures of the sampling location, raw laboratory results, and processed data will be reported. All data validation criteria will be reported along with deviations from the test setting requirements and associated comments related to these deviations.

6.2 Data Validation

Data validation is performed at the end of the project through an assessment of the Data Quality Indicators (DQIs) that are specific criteria used to quantify how well the collected data meet the Data Quality Objectives (DQOs). The measured DQI for the critical measurements will be compared to the defined DQOs set in this QAPP and that are consistent with the standards set forth in each respective referenced EPA Method.

6.3 Data Storage

Field data will be transferred from the HOBO data loggers to "data sticks" via a laptop computer with a USB port. Electronic data and pictures will be posted in the folder L:\Lab\NRML_Public\GullettResearchUpdates\WA 0-51 on the EPA network share drive upon return from the field or as it is generated or received.

7. Assessment and Oversight

7.1 Assessments and Response Actions

Assessments are an integral part of a quality system. This project is assigned a QA Category IV and does not require planned technical systems and performance evaluation audits. However, should deficiencies be identified by any of the key individuals responsible, an interoffice memorandum will be prepared and submitted to the ARCADIS and EPA project participants. The memorandum will discuss the problem and corrective actions taken. A QA performance evaluation will be performed to determine if DQIs goals were met for the overall project. Any internal audits performed by the ARCADIS QA staff will be followed by a written formal report to the ARCADIS WA Leader.

7.2 Reports to Management

All assessments performed by the EPA QA Representative or internally by the ARCADIS QA Officer will be formally reported to the EPA and ARCADIS WA Managers within 30 days. Findings from the audits will be reported immediately in order for any necessary corrective actions to be implemented.

The final report prepared for this project will contain a discussion of QA procedures and an evaluation of whether or not established DQI goals were met. In the event DQIs are outside of the acceptance criteria, the consequences of the failure to meet specific DQI goals will be discussed.

7.3 Corrective Actions

The ARCADIS WAL (Dr. A. Touati) is ultimately responsible for implementing corrective actions identified through QA Audits. An integral part of any QA program is well-defined procedures for correcting data quality problems. The overall goals of the QA program address the following aspects of data quality:

- Problem prevention
- Problem definition
- Problem correction

For this type of testing, data-quality problems usually require immediate, on-the-spot corrective action. The procedures outlined in this plan are intended to provide for rapid detection of data-quality problems. The experienced personnel assigned to this project will be intimately involved with the data on a daily basis. A data-quality problem will become apparent soon after it occurs. On-the-spot corrective actions will be taken when practical and are expected to be an everyday part of the QA process. The EPA WA Manager will be

notified promptly of QA problems that may require extended time for corrective action. The nature of the problem and corrective steps taken will be noted in the project notebook for future reference.

The ARCADIS QA Officer and the ARCADIS WAL will conduct regular inspections of project notebooks to assure completeness. Any discrepancies requiring prompt data quality problem correction will be resolved by the WAL. Through regular discussions with the project staff, the QA Officer and WAL will ascertain the continuing suitability of analytical systems performance. Because communications between project participants are open and frequent, this system is expected to be effective and will require a minimum amount of paperwork. The ARCADIS QA Officer will make documentation of problems requiring long-term solution.

8. References

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- EPA Method TO-13A" Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatographic/Mass Spectrometry (GC/MS) found in "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition" <http://www.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf>
- EPA Method 25C "DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES" <http://www.epa.gov/ttn/emc/promgate/m-25c.pdf>
- 40 CFR Part 50, Appendix J; "Reference Method for the Determination of Particulate Matter as PM10 in the Atmosphere;" 52 FR 24664, July 1, 1987; 52 FR 29467, Aug. 7, 1987 <http://www.epa.state.oh.us/portals/27/reqs/3745-25/3745-25-01.pdf>
- Compendium Method IO-3.3, "Determination Of Metals In Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy" in Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, June 1999. <http://www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-3-1.pdf>.
- METHOD TO-13A. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)



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NATA, 2002. Estimation of background concentrations for NATA 2002.

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Appendix B: Addendum to – QAPP for WP-2153 Work



Addendum to:

**Determination of Emission Factors from Open Burning and Open
Detonation of Military Ordnance**

2011 Open Burning Tests

Quality Assurance Project Plan
Category IV / Proof of Concept

March 12, 2011

Brian Gullett U.S. Environmental Protection Agency Principal Investigator, Grantee Mentor, and Work Assignment Manager	Date
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Dennis Tabor U.S. Environmental Protection Agency Analytical Leader	Date
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Johanna Aurell NRC Grantee, Post-Doctoral Fellow to the U.S. EPA Technical Project Leader	Date
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Dahman Touati ARCADIS Work Assignment Leader	Date
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Paul Groff or Robert Wright U.S. Environmental Protection Agency Quality Assurance Representative	Date
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Laura Nessley ARCADIS Quality Assurance Officer	Date
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Introduction

This is an addendum to the QAPP entitled “Determination of Emission Factors from Open Burning and Open Detonation of Military Ordnance” allowing for additional work scheduled for Spring, 2011. The Department of Defense’s Strategic Environmental Research and Development Program (SERDP) has awarded second year funding to further pursue development of methods for emission characterization of open burning of military propellants. This additional work will focus on multiple propellant types whose composition varies from that of the first year propellant, M1. Tests this year will develop and test additional methods of sampling to characterize these propellants and are based on input from the U.S. Army’s Defense Ammunition Center (DAC) and their advisors. New target analytes this year will include perchlorate, chloride, and hydrogen chloride from Cl-containing propellants and additional metals (e.g., Ba) from other propellants. In addition, repeat samples and analyses will be conducted to further develop these sampling methods. All tests will be conducted at the Tooele (Utah) Army Depot test range, the site of the 2010 tests.

This addendum is meant as an addition to the cited QAPP. Differences in test materials, target analytes, sampling and analytical methods, and burn procedures are included.

Schedule

February 18, 2011	Draft QAPP Addendum submitted to EPA and to U.S. Army DAC
March 4, 2011	QAPP Reviewed
March 20, 2011	Team arrives in Tooele
March 21 – April 8, 2011	Field Testing
August, 2011	Draft report
September, 2011	Final report

Propellants

Five Propellants will be tested by Open Burning (OB). These propellants and their composition are listed in Table A1. This table is an amendment to Table 3-1, “Composition of OB and OD Ordnance,” in the original QAPP. These propellants were selected by the U.S. Army DAC with criterion of stockpile relevance, method gaps, and emission factor data gaps. Two propellants (of three currently listed) will be selected for their composition of ammonium perchlorate (over 65% by mass). Their OB plumes will be sampled for perchlorate, HCl, and chloride salts. Three propellants were also selected that represent single, double, and triple base compositions. Two of these, M31A1E1 and SPCF, contain metals (barium and lead, respectively) which will enable testing of PM-based metal capture and detection. Note: selection of the ammonium perchlorate propellants is not finalized; these three are examples of potential candidates. At least two perchlorate-based propellants are targeted for testing.

Charge sizes in 2011 will be increased to 200 lbs and will continue to be ignited in metal burn pans. If meteorological conditions permit (e.g., wind speed and cloud cover), up to 300 lbs can be tested in a single charge. The advantage of the larger charge size is the proportionately higher concentration of target analytes in the plume and the greater ease with which limits of detection can be exceeded.

Table A1. Target Propellants.

Propellant Name	Propellant Descriptor	Mass %	Component, CAS #, Chemical formula****	
M31A1E1	Triple Base	To be provided by DAC	Nitrocellulose Nitroglycerin Nitroguanidine	9004-70-0 55-63-0 556-88-7
M26	Double Base	To be provided by DAC	Nitrocellulose Nitroglycerin Barium nitrate Potassium nitrate	9004-70-0 55-63-0 10022-31-8 7757-79-1
SPCF	Single Base	To be provided by DAC	Nitrocellulose Lead carbonate	9004-70-0 598-63-0
ANP-3196-1*	Hawk Sustainer	60-75 15-20	Ammonium Perchlorate (AP) Nitroguanidine	7790-98-9 556-88-7
ANP-3146-1**	Hawk Booster	60-70 15-20	Ammonium Perchlorate (AP) Aluminum powder	7790-98-9 7429-90-5
AnB-3745; ANB-3748 (igniter)***	Atlas V Propellant and igniter	67-70 18-20 0-1 0-1	Ammonium Perchlorate (AP) Aluminum Powder Triphenyl Bismuth (TPB) Iron Oxide (in igniter)	7790-98-9 7429-90-5 603-33-8 1309-37-1

* Information obtained from AEROJET MSDS NO. 501, Revision 5.

** Information obtained from AEROJET MSDS NO. 500, Revision 3

*** Information obtained from AEROJET MSDS NO. 13003, Revision 3

****Composition of propellants limited to propellants, explosives, and pyrotechnic (PEP) materials and Metals

Changes to the Flyer

A number of advances were made to the sampling instrumentation package, or the “Flyer.” Two Flyers now exist, “Orville” and “Wilbur.” Both consist of a lightweight, aluminum frame structure which replaced the solid aluminum structure of the original Flyer. Orville was outfitted with a telemetry system to transmit data to a handheld station. Orville’s telemetry system enables the ground crew to monitor CO₂ concentration, battery life, and pressure drop across a filter. These data allow maximization of flight time and optimization of collection by avoiding premature battery changeouts or battery depletion and allowing for filter changes when plugged. Orville was used in July 2010 when monitoring the in situ oil burns at the BP Gulf oil spill.

Wilbur lofts a computer and control software in lieu of the telemetry system. This computer enables data storage like the original Flyer but also allows the sampling to be controlled from the ground and allows the incorporation of multiple triggers. These multiple triggers, for example, allow one to loft multiple summa canisters and trigger, or open, them at different CO₂ concentrations.

A number of other changes are included in both systems. The Ni-Cd batteries were replaced with Li-ion. The 6 L summa canister was replaced with a lighter 1L canister. The semivolatile blower was replaced with a unit that has about four times the flowrate of the old system, up to about 650 L/min. An electrochemical cell for real time CO was added. Continuous PM samplers and black carbon samplers are also optional.

New Target Analytes

Section 3.2 “Analytes and Process Measurements” of the QAPP is amended to include additional analytes and their measurements as well as changes (shown in italics) in Table A2. Emissions to be measured in 2011 will include CO₂, CO, PM₁₀ and PM_{2.5}, metals (e.g., Pb, Al, and Ba), VOCs, SVOCs, HCl, ClO₄⁻, and other chlorinated compounds.

Table A2. Target compounds and sampling and analysis methods (new methods or changed methods in italics).

Target Compound	Sampling Method	Sampling Rate	Analysis
VOCs	TO-15 Summa	30 s (from 2-3 L/min)	GC/LRMS
SVOCs	TO-13, PUF/XAD-2/PUF	650 L/min (from 200 L/min)	GC/LRMS
<i>PM_{2.5} and PM₁₀</i>	<i>Filter</i>	<i>10 L/min</i>	<i>Analytical Balance</i>
<i>HCl</i>	<i>Alkali-impregnated filters, silica gel tubes</i>	<i>2-4 L/min</i>	<i>Ion chromatography</i>
<i>Carbon monoxide</i>	<i>EPA Method 25C chemical cell</i>	<i>150 mL/min</i>	<i>GC</i>

Measurement Methods for New Target Analytes

Perchlorate will be sampled using a modification of the method discussed in Lamm et al. (1999). The method consists of sampling at a flowrate of 2 L/min through a 37 mm mixed cellulose ester (MCE) filter (0.8 µm pore size) enclosed in a closed-face cassette (SKC Corporation). Perchlorate salts are captured as a solid on the filter, which assumes no perchloric acid formation. Cassette samples will be dissolved/extracted in water, an internal standard added, and then analyzed for perchlorate with LCMS and chloride with ion chromatography as per U.S. EPA SW-846 Method 6850. Samples will be analyzed at Columbia Analytical Services (CAS, NY).

The detection limit for perchlorate is cited as 0.004 µg/filter by CAS (NY). For the purposes of determining required sampling volumes and times to reach perchlorate detection levels, we first assume 100% preservation of the original perchlorate composition as a best case boundary condition and dilution at the Flyer sampler at the ratio observed for C to CO₂ during the 2010 tests. Calculations were done using M7 propellant, containing 8 weight percent potassium perchlorate, as this was indicated early on as a candidate for the testing. The average 2010 sampled concentration of CO₂ from M1 was 460 ppm (against a background of ~ 390 ppm) from a carbon fraction of 30 wt percent in the propellant. From these ratios, the maximum possible concentration of perchlorate we can expect in the M7 plume would be 80 ppm (124 mg/m³). At a sampling rate of 2 L/min, we could expect to collect 0.25 mg/min. When compared against a reported detection limit of 0.004 µg/filter, the required sampling time to reach detection is significantly less than 1 sec. As of February 2011, the expected perchlorate propellants contain >60% ammonium perchlorate, considerably more than the M7 we used for these calculations. Even if only ca. 5% of the original perchlorate is released intact and is diluted to levels below 80 ppm in the plume, sampling for detectable perchlorate should be relatively fast.

The perchlorate may also degrade into chlorine which could react with alkaline earth metals, either within the propellant or entrained from the surrounding soil, to form a metal chloride. Lindsay et al. (1999) noted that HCl could readily be absorbed by entrained soil as well as aluminum oxide from the propellant. These metal chlorides will be captured on the initial perchlorate filter and analyzed by ion chromatography from the same filter.

We also will sample for formation of HCl. Methods for sampling HCl are primarily derived from those intended for sampling inhalable HCl to relate to exposure risk. Silica gel collection methods such as NIOSH Method 7903 (NIOSH 1994) may undersample HCl mist, as particle size collection characteristics on the silica gel sorbent tube do not match the inhalable convention (Howe et al., 2006). While there are considerable questions relating to the relevance of these methods to the inhalable particle/droplet size (Howe et al., 2006), our effort is more concerned with complete capture and quantification. HCl will be sampled in parallel using alkali-impregnated filters following the perchlorate filter and silica gel tubes as per Lindsay et al. (1999). HCl gas is expected to pass through the perchlorate/chloride filter and be adsorbed by a second, quartz filter coated with Na_2CO_3 . These coated filters are available in a cartridge from SKC Corporation. Any hydrochloric acid transiently collected on the initial filter is expected to rapidly evaporate and be collected along with the gaseous HCl (Howe, et al. 2006). This method, including a prefilter followed by a Na_2CO_3 -impregnated quartz filter, is consistent with a method from France (INRS, 2002), as cited in Howe et al. (2006).

Numerous tests on the prefilter/ Na_2CO_3 -impregnated quartz filter method were covered by Howe et al., (2006). They examined pre-filter HCl vapor capture and breakthrough potential. The former did not exceed 0.4% and the latter were all non-detect after collection of 47 to 62 μg of chloride on the alkaline filters. The pre-filter did have a propensity to collect significant HCl when doped with Fe, Fe_2O_3 , or ZnO suggesting an underestimation of HCl from the Na_2CO_3 -impregnated quartz filter alone when in the presence of propellants metals (e.g., Al from Atlas Igniter propellant) or plume-entrained soil. The extent to which this may relate to our work is uncertain; the experiments of Howe et al. did not control for the amount of dopant on the filter.

This filter will be analyzed for HCl by ion chromatography methods specified in EPA Method 26. The limit of detection for this method is 4 μg /filter (CAS, NY). Assuming that all of the M7 propellant's perchlorate becomes HCl, and assuming a dilution ratio consistent with the 2010 dilution of CO_2 , we anticipate a maximum possible HCl concentration of 30 ppm or 45 mg/m^3 . Lindsay et al. (1999) noted that their silica gel tube method did not detect gaseous HCl at levels above 6.5 mg/m^3 (the background contamination level of the silica gel tubes). At a sampling flowrate of 2 L/min, we will need 2.4 s to reach the 4 μg /filter level, assuming a concentration of 30 ppm HCl in the plume. If our plume HCl concentration is actually seven times lower than 30 ppm, equivalent to the 6.5 mg/m^3 background level noted by Lindsay et al., this will be compensated by the higher Cl concentration in our targeted propellants as compared to M7. Nonetheless, we anticipate sampling for approximately 300 s (one day) to obtain a composite sample for HCl analysis.

The perchlorate prefilter and Na_2CO_3 filter both will be analyzed for target analytes prior to sampling at Tooele in order to establish contamination levels. Ambient air background levels will be determined for perchlorate, chloride, and HCl. Moller and Acker (2007) found HCl concentration maxima around noon of 0.1 $\mu\text{g}/\text{m}^3$, dropping 10-fold at night. They also found an average of 50% of the total Cl mass as gas-phase HCl.

In 2010, only PM_{10} was collected for dust loading and metal analysis. In 2011, $\text{PM}_{2.5}$ and PM_{10} sampling will be performed simultaneously using two 47 mm tared Teflon filters each with a SKC Leland Legacy sample pump with a constant airflow of 10 L/min. The internal flow sensor measures flow directly and acts as a secondary standard to constantly maintain the set flow. The volume display is continually updated, based on corrected flow rate multiplied by sampling time. The pump operation is controlled by

the CEM CO₂ trigger circuit. The SKC Leland Legacy Sample pump will be calibrated before and after the sampling campaign, with a Gilibrator Air Flow Calibration System (Scientific Instruments), which is a primary standard airflow calibrator.

PM will be measured gravimetrically as the difference between final and tare masses for each filter. The weighing of the filters will follow the procedures described in (40 CFR Part 50, 1987). Calibration for determining mass of conditioned media will be performed as described in Quality Assurance Guidance Document 2.12 (USEPA, 1998). The PM collected on Teflon filters will also be used to determine concentrations of target metals such as Pb and Al. EPA Compendium Method IO-3.3 (USEPA, 1999c) specifies the analysis by energy dispersive x-ray fluorescence spectrometry (EDXRF). This method is compatible with particulate on filters, is quite sensitive for metals, and is non-destructive. This means that the PM and substrate survive the analysis intact and may be archived or analyzed by other methods. Select PM samples from non-metal-containing propellants will be sampled for metals to determine whether the burn pans are sources of residual metal carryover.

Carbon monoxide will be sampled continuously using a semi-real time monitor. An onboard CO sensor (Creative Solutions RCO1000) will measure CO concentration by means of an electrochemical cell through CO oxidation. Output is linear from 0 to 1000 ppm at an operating RH range of 15-90%. The RCO 1000 will be calibrated in the EPA Metrology Laboratory prior to departure at 0 to 100 ppm with ± 2 ppm error using EPA method 3A (2008). CO measured by flow through chemical cell will be corroborated by the measurement of a sample taken from the Summa canister system and analyzed via gas chromatography.

2010 Measurements

Other measurements conducted in 2010, such as VOC analysis (e.g., benzene) and SVOC analysis (e.g., naphthalene) will be repeated in 2011 tests. In general, emission factors determined in 2010 agreed well with published data. Additional tests in 2011 will serve the primary purpose of defining the range and variability of the sampling/analytical methods. These data will be useful if the DoD wishes to further establish methods that will be used in future regulatory- or permit-related testing.

One change to the 2010 analyses will be the inclusion of additional semivolatiles including nitroaromatic energetics. CAS (NY) will analyze for nitroglycerin (when present in the propellant) by high performance liquid chromatography (EPA Method 8332). Nitrocellulose can be analyzed by a total nitrogen method, but is probably not sufficiently sensitive for our samples, so will not be targeted. Additional commercial analytical sources are still being sought at the time of this writing. EPA will analyze for nitroaromatics (nitrotoluene and nitrobenzene) and PAHs by a EPA Method 8270. The method is modified by use of selective ion monitoring (SIM) with GC/LRMS to get lower detection limits, inclusion of nitrotoluene as a target analyte, and adjustment of the extraction volumes or dilution of the extract to get concentrations inside the calibration range. NitroPAHs will not be analyzed.

Ash

After each 6-pan burn series, the propellant ash will be collected and weighed. Samples of ash will be gathered from the burn pans for each propellant type and analyzed for original constituent metals such as Pb and Ba and residual energetics. Non-Pb- and non-Ba-containing propellant ash will also be examined to ascertain the potential for carryover between propellants. Limited PM filters from non-metal-containing propellants will likewise be analyzed for metal carryover.

Test Matrix

Our plan is to sample approximately 18 burns per day (three series of six pans with 200 lbs each), providing for 300+ seconds of sampling per day (the 2010 average was 17 sec per burn). The order of the propellant testing is dependent on the arrival and availability of propellant at Tooele, which was still to be determined as of 3/12/2011. Table 3-4 of the original QAPP is amended as follows:

Day	Propellant	Pans*Wt	ClO ₄ , Cl, HCl	VOC, Summa	Semi-volatiles, PUF/XAD-2/PUF	PM _{2.5} , PM ₁₀ , metals	CO and CO ₂
1	Type	Series*pans*weight	Field blank	Field blank	Field blank	Field blank	Background (upwind)
			Background (upwind, lofted)	Background (upwind, lofted)	Background (upwind, lofted)	Background (upwind, lofted)	Background (upwind, lofted)
2, 3	AP1	2*6*200 lb		@ 12 Pans	X	@ 6 Pans	X
		4*6*200 lb	@ 6 Pans (see below)		X	@ 6 Pans, PM2.5 only	X
4, 5	SB	3*6*200 lb	NA	@ 12 Pans	X	@ 12 Pans	X
		3*6*200 lb					X
6, 7	DB	3*6*200 lb	NA	@ 12 Pans	X	@ 12 Pans	X
	DB	3*6*200 lb					X
8, 9	TB	3*6*200 lb	NA	@ 12 Pans	X	@ 12 Pans	X
	TB	3*6*200 lb					X
10, 11	AP2	2*6*200 lb		@ 12 Pans	X	@ 6 Pans	X
		4*6*200 lb	@ 6 Pans (see below)		X	@ 6 Pans, PM2.5 only	X
12, 13	backup						
14	OD tests	Trial survivability tests for aerostat with shrapnel detonations					
15	cleanup						

AP1, AP2 = ammonium or potassium perchlorate (TBD) #1, #2; NA = not applicable; SB = single base; DB = double base; TB = triple base; OD = open detonation.

CI Matrix for Each AP Propellant

Four six-pan series will be tested for primary analytes (bold) and secondary analytes using the cartridge and silica methods in parallel as follows:

# pans, wt	Cartridge Method			Silica Method	
	MCE filter	H ₂ SO ₄ -treated filter	Na ₂ CO ₃ -treated filter	MCE filter	Silica gel tube
6* 200 lbs	Perchlorate , chloride	—	HCl , perchlorate	—	HCl
6* 200 lbs	Perchlorate , chloride	Cl₂	HCl , perchlorate	Perchlorate , chloride	HCl
6* 200 lbs	Perchlorate , chloride	—	HCl	—	HCl
6* 200 lbs	Perchlorate , chloride		HCl , HCl (2 filters in series)	Perchlorate , chloride	HCl

The combination of these methods will allow us to compare the cartridge and silica methods for HCl (quantity and variance of data), determine perchlorate concentration and analyze for perchlorate vapor “slip” onto the Na₂CO₃ filter, evaluate chloride deposition on the MCE filter, look for HCl breakthrough, and evaluate the presence of Cl₂.

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<http://www.cdc.gov/niosh/nmam/>

Appendix C: Addendum #2 to – QAPP for WP-2153 Work



Addendum #2 to:

Determination of Emission Factors from Open Burning and Open Detonation of Military Ordnance

2011 CI Species Method Tests

Quality Assurance Project Plan
Category IV / Proof of Concept

June 21, 2011

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Introduction

This is an addendum to the QAPP entitled "Determination of Emission Factors from Open Burning and Open Detonation of Military Ordnance" relating to additional work scheduled for the Summer and Fall of 2011. In 2010 the Department of Defense's Strategic Environmental Research and Development Program (SERDP) awarded second year funding to further pursue development of methods for emission characterization of open burning of military propellants. This additional work focused on multiple propellant types including an ammonium perchlorate (AP) propellant with target analytes of perchlorate, chloride, and hydrogen chloride from the Cl-containing propellants. Methods for sampling these Cl-based analytes were derived from indoor and personal sampling methods and were covered in a previous addendum dated April, 2011. This field sampling was apparently successful, but the tests were limited in number. Further, the potential for breakthrough of the analytes could not be assessed based on the setup used at Tooele. The scope of this additional work relates to further testing of the same sampling methods detailed in Addendum #1. This additional testing will allow methods development with parallel samplers, control of flow rates, sample size, and simultaneous methods evaluation. The work on HCl testing will be done at the US EPA facilities at Research Triangle Park and the AP burns will be done at the U.S. Navy's Naval Surface Warfare Center (NSWC) in Indian Head, Maryland. The work at NSWC is being sponsored by the U.S. Army Defense Ammunition Center (DAC).

Schedule

June 24, 2011	Draft QAPP Addendum submitted to EPA with copies to U.S. Army DAC and NSWC
July 1, 2011	QAPP reviewed and approved.
July 12, 2011	HCl testing at RTP or AP testing at NSWC
August 8 or 15, 2011	Alternate date for AP testing at NSWC
October 7, 2011	Draft report/paper to DAC and to EPA review
November 30, 2011	Final report/paper

Method

HCl Sampling

Methods for sampling HCl are primarily derived from those intended for sampling inhalable HCl to relate to exposure risk. Methods consist of a filter method (ISO Method 21438-2) and silica gel tube method (NIOSH 1994). Tests done with HCl at the EPA's RTP laboratories will evaluate the sorptive capacity and breakthrough limits of an alkali-impregnated filter and silica gel methods.

HCl will be sampled in parallel using 1) alkali-impregnated filters following a solid perchlorate filter and 2) silica gel tubes as per Lindsay et al. (1999). HCl gas is expected to pass through the first perchlorate/chloride filter and be adsorbed by a second, quartz filter coated with Na_2CO_3 . These coated filters are available in a cartridge from SKC Corporation. Any hydrochloric acid transiently collected on the initial filter is expected to rapidly evaporate and be collected along with the gaseous HCl (Howe, et al. 2006). This method, including the prefilter followed by a Na_2CO_3 -impregnated quartz filter, is consistent with a method from France (INRS, 2002), as cited in Howe et al. (2006) and became a European standard method 2009 (ISO Method 21438-2).

Silica gel collection methods such as NIOSH Method 7903 (NIOSH 1994) may undersample HCl mist, as particle size collection characteristics on the silica gel sorbent tube do not match the inhalable convention (Howe et al., 2006). While there are considerable questions relating to the relevance of these methods to the inhalable particle/droplet size (Howe et al., 2006), our effort is more concerned with complete capture and quantification.

The NIOSH silica gel tube method is written based on flowrates of 0.2-0.5 L/min. Because of the brief time available to sample rocket plumes in the field, a faster volumetric sampling rate, up to 1.5 L/min, is desired. However, we need to test the breakthrough capacity in order to guard against falsely low measurements in the field.

The work covered here will involve feeding known concentrations of HCl gas through the filter cassette (SKC model 225-9005) and silica gel tube while measuring breakthrough versus flowrate and concentration. HCl gas will be metered via a mass flow controller and will target concentrations seen in the field during sampling (ca. 20 ppm). Feed HCl gas will be monitored at the beginning of the test and exit gas will be monitored throughout the test with the Bodenseewerk analyzer. These tests will determine the ability of the NIOSH method to extend to higher flowrates without breakthrough. A few tests will be monitored with Draeger diffusion tubes (1.3 – 200 ppm) in anticipation of their use at subsequent Indian Head tests. Test conditions are shown in the table below.

Table 1. HCl test matrix (work done at RTP, NC).

Method	Flow rate (L/min)	HCl concentrations (ppm)	Time (min)
ISO Method 21438-2, filter method	4	N2 only	1
	4	N2 only	5
	4	< 20	1
	4	< 20	5
	4	50	1
	4	50	5
	10	N2 only	1
	10	N2 only	5
	10	< 20	1
	10	< 20	5
	10	50	1
	10	50	5
NIOSH Method 7903, silica gel tube method	1.5	N2 only	1
	1.5	N2 only	5
	1.5	< 20	1
	1.5	< 20	5
	1.5	50	1
	1.5	50	5

Select filters may be analyzed for HCl by ion chromatography methods specified in EPA Method 26 as a check. These analyses will likely be performed by CAS (NY) as with the Tooele Year 2 samples; their limit of detection for this method is 4 µg/filter.

Perchlorate, Chlorate, Chloride Sampling

A single type of ammonium perchlorate (AP, over 65% by mass) propellant available at NSWC Indian Head will be tested in their facilities. A small amount (5 to 25 g) of AP will be burned in an enclosed, vented hood (see photo). The hood is approximately 48 ft³ in size. Its emissions are vented to the outside. The emissions from the AP burn will be sampled by EPA with up to four samplers at once, testing the two different methods, the filter-based ISO method and the silica gel NIOSH method. The ventilation rate of the hood will be reduced during the burns to increase the residence time of the AP gases within the hood, allowing for greater capture by the samplers. The target analytes will include perchlorate, chlorate ion, HCl, and chloride salts. The samplers will be those used in the April 2011 Tooele testing (Figure 1).

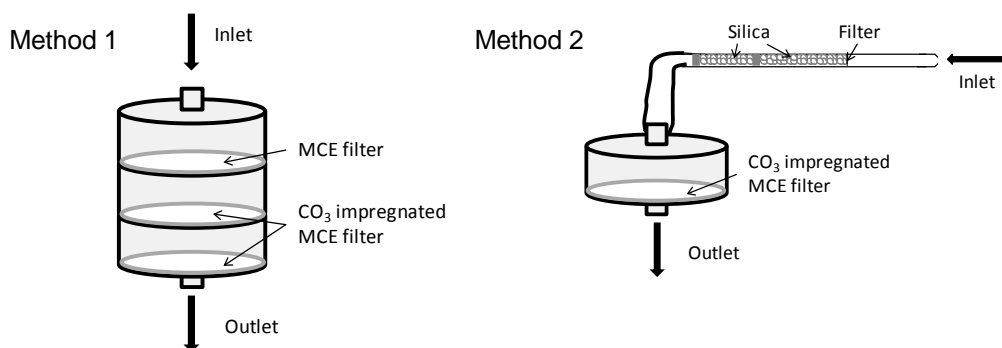


Figure 1. Sampling apparatus for HCl, perchlorate, and chlorate. Method 1 (ISO 21438-2) followed by a second additional CO₃ filter at the left and method 2 (NIOSH 7903), followed by a CO₃ filter, at the right.

Perchlorate will be sampled using a modification of the method discussed in Lamm et al. (1999). The method consists of sampling at a flowrate of 2 L/min through a 37 mm mixed cellulose ester (MCE) filter (0.8 µm pore size) enclosed in a closed-face cassette (SKC Corporation). Perchlorate salts are captured as a solid on the filter, which assumes no perchloric acid formation. Cassette samples will be dissolved/extracted in

water, an internal standard added, and then analyzed for perchlorate with LCMS and for chloride with ion chromatography as per U.S. EPA SW-846 Method 6850. Samples will be analyzed at Columbia Analytical Services (CAS, NY).

The detection limit for perchlorate is cited as 0.004 µg/filter by CAS (NY). For the purposes of determining required sampling volumes and times to reach perchlorate detection levels, we used the chlorate ion emission factor derived at Tooele 2011, 1.0 E-06 g/g ClO₃⁻. In order to reach 5 or 10 times the method reporting limit with a propellant size of 5 g we need to sample for 4 or 8 minutes, respectively, with a flow rate of 4 L/min. Table 2 shows the test matrix including the similarly calculated sampling times to reach 5 or 10 times the detection levels.

We also will sample for formation of HCl using the filter and silica gel tube methods indicated above during the Indian Head tests. HCl will be sampled in parallel using alkali-impregnated filters following the perchlorate filter and silica gel tubes as per Lindsay et al. (1999). HCl gas is expected to pass through the perchlorate/chloride filter and be adsorbed by a second, quartz filter coated with Na₂CO₃. These coated filters are available in a cartridge from SKC Corporation. This filter will be analyzed for HCl by ion chromatography methods specified in EPA Method 26.

Ambient air background levels will be determined for perchlorate, chloride, and HCl.

Table 2. Perchlorate, chlorate, and HCl Test Matrix

Method	Propellant amount (g)	Flow rate (L/min)	Time (min)	X ClO ₄ /3 Det Limit
Lamm et al. (1999) and	5	4	4	5
ISO Method 21438-2	5	10	2	5
	5	4	8	10
	25	4	2	10
	25	10	1	10
	Background	4	60?	
	Background	10	60?	
NIOSH Method 7903	5	1.5	2	NA
	25	1.5	1	NA
	Background	1.5	60?	

Background sampling times to achieve the detection limit are unknown.

NA = HCl values only can be determined.

The combination of these methods will allow us to compare the cartridge and silica methods for HCl (quantity and variance of data), determine perchlorate concentration, analyze for perchlorate vapor “slip” onto the Na₂CO₃ filter, evaluate chloride deposition on the MCE filter, and look for HCl breakthrough.

The sampling times in Table 2 rely on our preliminary emission factors determined at Tooele in 2011 and so assume that the small scale AP tests at Indian Head will yield Cl species in a proportionate manner. Another confounding factor is the evacuation rate of the Indian Head chamber. To guard against these unknowns, CO₂ will also be monitored in the Indian Head chamber to monitor pollutant depletion using the same Li-COR sampler as used at Tooele. Further assurance of the target levels inside the chamber will be determined qualitatively by monitoring HCl using Draeger diffusion tubes. The sampling times will be adjusted accordingly to achieve the desired ratio above the detection limit.

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<http://www.cdc.gov/niosh/nmam/>

Appendix D: Data for Each Sample Collected

All EFs are ambient air background corrected.

Table D1. Number of samples collected for each propellant type.

Propellant type	PM2.5	PM10	SVOC	VOC	HCl/perchlorate/chlorate
M31A1E1	3	3	2	4	0
M26	2	2	1	5	0
SPCF	2	2	2	3	0
Sparrow Rocket Motor	0	1	1	1	2

Table D2. SVOC Emission factor for each collected sample.

	M31A1E1 lb/lb Carbon	M31A1E1 lb/lb Carbon	M26 lb/lb Carbon	SPCF lb/lb Carbon	SPCF lb/lb Carbon	AP Static lb/lb Carbon
Nitrobenzene	5.6E-06	2.5E-06	1.4E-07	ND	ND	ND
Nitrotoluenes	2.1E-07	ND	ND	ND	ND	ND
Naphthalene	6.9E-06	6.5E-06	1.2E-07	7.8E-08	1.3E-07	8.4E-07
Acenaphthylene	1.6E-07	2.6E-07	2.9E-08	8.3E-10	4.2E-08	5.3E-08
Acenaphthene	8.8E-08	1.5E-07	8.5E-09	6.6E-09	1.2E-08	ND
Fluorene	5.8E-07	6.0E-07	3.3E-08	1.8E-08	4.5E-08	1.6E-07
Phenanthrene	3.2E-07	8.9E-07	6.2E-08	5.4E-08	1.5E-07	5.5E-07
Anthracene	2.4E-08	7.3E-08	3.8E-09	2.2E-09	1.3E-08	5.7E-08
Fluoranthene	3.3E-08	1.3E-07	1.7E-08	1.2E-08	2.9E-08	1.9E-07
Pyrene	2.5E-08	1.0E-07	1.2E-08	9.5E-09	2.3E-08	ND
Benzo(a)anthracene	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	9.3E-09	ND
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND	ND
Benzo(ghi)perylene	ND	ND	ND	ND	ND	ND

ND = Not detected, ND values were ignored when calculating the EFs. Detection Limit- The concentration of a compound where the peak height is 2.5 times the height of the peak-to-peak noise, see Table D3 for detection limits.

Table D3. SVOC concentration and concurrent amount of carbon in each sample.*

	Ambient air	M31A1E1	M31A1E1	M26	SPCF	SPCF	AP Static
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
Nitrobenzene	ND [0.13]	1439 [3.6]	762 [11]	33 [3.2]	ND [3.1]	ND [9.6]	ND [25]
Nitrotoluenes	ND [0.33]	55 [8.8]	ND [28]	ND [7.8]	ND [7.6]	ND [23]	ND [61]
Naphthalene	0.57 [0.017]	1790 [0.46]	1996 [1.4]	28 [0.41]	17 [0.39]	31 [1.2]	48 [3.2]
Acenaphthylene	0.072 [0.038]	42 [1.0]	81 [3.2]	6.9 [0.91]	0.25 [0.88]	9.7 [2.7]	3.0 [7.1]
Acenaphthene	0.072 [0.022]	23 [0.60]	45 [1.9]	2.0 [0.53]	1.4 [0.51]	2.9 [1.6]	ND [4.1]
Fluorene	0.23 [0.019]	149 [0.51]	184 [1.6]	8.0 [0.45]	4.0 [0.44]	11 [1.4]	9.0 [3.5]
Phenanthrene	0.45 [0.011]	84 [0.28]	274 [0.9]	15 [0.25]	12 [0.24]	36 [0.75]	32 [2.0]
Anthracene	0.024 [0.012]	6.1 [0.31]	22 [1.0]	0.91 [0.28]	0.50 [0.27]	2.9 [0.83]	3.2 [2.2]
Fluoranthene	0.078 [0.044]	8.6 [1.2]	40 [3.7]	4.0 [1.1]	2.6 [1.0]	6.7 [3.2]	11 [8.2]
Pyrene	0.054 [0.022]	6.6 [0.60]	31 [1.9]	2.9 [0.53]	2.1 [0.52]	5.5 [1.6]	ND [4.1]
Benzo(a)anthracene	ND [0.031]	ND [0.85]	ND [2.7]	ND [0.75]	ND [0.73]	ND [2.2]	ND [5.8]
Chrysene	ND [0.026]	ND [0.69]	ND [2.2]	ND [0.61]	ND [0.59]	2 [1.8]	ND [4.8]
Benzo(b)fluoranthene	ND [0.022]	ND 0.60]	ND [1.9]	ND [0.53]	ND [0.52]	ND [1.6]	ND [4.1]
Benzo(k)fluoranthene	ND [0.045]	ND [1.2]	ND [3.8]	ND [1.1]	ND [1.0]	ND [3.2]	ND [8.4]
Benzo(a)pyrene	ND [0.046]	ND [1.2]	ND [3.8]	ND [1.1]	ND [1.0]	ND [3.2]	ND [8.4]
Indeno(1,2,3-cd)pyrene	ND [0.033]	ND [0.89]	ND [2.8]	ND [0.79]	ND [0.76]	ND [2.3]	ND [6.1]
Dibenz(a,h)anthracene	ND [0.049]	ND [1.3]	ND [4.1]	ND [1.2]	ND [1.1]	ND [3.5]	ND [9.1]
Benzo(ghi)perylene	ND [0.0056]	ND [0.15]	ND [0.48]	ND [0.13]	ND [0.13]	ND [0.40]	ND [1.0]
Carbon (mg/m ³)	NA	257	306	232	216	231	56

* ND=Not detected, detection limit within parentheses. NA – not applicable.

Table D4. PM EF for each collected sample, in lb/lb NEW.*

	Sample #	PM2.5	Sample #	PM10
M31A1E1	1	3.5E-03	1	4.5E-03
	2	3.2E-03	2	3.5E-03
	3	4.0E-03	3	3.9E-03
M26	1	1.1E-02	1	1.1E-02
	2	1.2E-02	2	1.1E-02
SPCF	1	1.5E-02	1	1.4E-02
	2	1.5E-02	2	1.5E-02
AP Static	1	NS	1	1.5E-01

*NS – Not Sampled.

Table D5. PM concentration and amount carbon collected in each sample.*

	Sample #	PM2.5	Carbon	Sample #	PM10	Carbon
		$\mu\text{g}/\text{m}^3$	mg/m^3		$\mu\text{g}/\text{m}^3$	mg/m^3
M31A1E1	1	5174 [24]	265	1	6522 [24]	265
	2	5576 [25]	319	2	6192 [25]	319
	3	6850 [24]	314	3	6802 [24]	314
M26	1	11771 [17]	279	1	11742 [17]	279
	2	7345 [24]	155	2	6675 [24]	155
SPCF	1	11703 [14]	207	1	11155 [14]	207
	2	12475 [11]	219	2	12475 [11]	219
AP Static	1	NS	NS	1	32909 [91]	24
Ambient air	1	17 [0.41]	NA	1	15 [0.41]	NA

* NS – Not Sampled. Detection limit within parentheses. NA – not applicable.

Table D6. Metal EF for each collected sample, in lb/lb NEW.*

	Sample #	PM2.5 K	PM2.5 Ba	PM2.5 Pb	Sample #	PM10 K	PM10 Ba	PM10 Pb	PM10 Al	PM10 Fe	PM10 Mo
M31A1E1	1	7.0E-04	NA	NA	1	7.5E-04	NA	NA	NA	NA	NA
	2	8.4E-04	NA	NA	2	9.0E-04	NA	NA	NA	NA	NA
	3	9.3E-04	NA	NA	3	9.8E-04	NA	NA	NA	NA	NA
M26	1	1.8E-03	2.5E-03	NA	1	1.8E-03	2.6E-03	NA	NA	NA	NA
	2	1.7E-03	2.5E-03	NA	2	1.7E-03	2.6E-03	NA	NA	NA	NA
SPCF	1	2.3E-03	NA	6.0E-03	1	2.3E-03	NA	6.0E-03	NA	NA	NA
	2	2.5E-03	NA	6.3E-03	2	2.5E-03	NA	6.3E-03	NA	NA	NA
AP Static	1	NS	NS	NS	1	8.2E-04	NS	NS	1.2E-02	5.3E-03	4.9E-03

* NS=Not sampled. NA=Not analyzed.

Table D7. Metal concentration in each collected sample in $\mu\text{g}/\text{m}^3$.*

	Sample #	PM2.5 K	PM2.5 Ba	PM2.5 Pb	Sample #	PM10 K	PM10 Ba	PM10 Pb	PM10 Al	PM10 Fe	PM10 Mo
M31A1E1	1	1020 [4.8]	NA	NA	1	1093 [4.8]	NA	NA	NA	NA	NA
	2	1468 [4.9]	NA	NA	2	1574 [4.9]	NA	NA	NA	NA	NA
	3	1598 [4.9]	NA	NA	3	1693 [4.9]	NA	NA	NA	NA	NA
M26	1	1976 [3.4]	2751 [0.55]	NA	1	1993 [3.4]	2854 [0.55]	NA	NA	NA	NA
	2	1066 [4.8]	1520 [0.77]	NA	2	1073 [4.8]	1571 [0.77]	NA	NA	NA	NA
SPCF	1	1853 [2.8]	NA	4769 [2.8]	1	1824 [2.8]	NA	4811 [2.8]	NA	NA	NA
	2	2113 [2.2]	NA	5307 [2.2]	2	2113 [2.2]	NA	5362 [2.2]	NA	NA	NA
AP Static	1	NS	NS	NS	1	182 [18]	NS	NS	2739 [54]	1172 [7.3]	1082 [7.3]
Ambient air	1	0.43 [0.083]	ND [0.013]	ND [0.083]	1	0.47 [0.083]	0.052 [0.013]	ND [0.083]	1.3 [0.25]	0.24 [0.033]	ND [0.033]

* ND=Not detected, detection limit within parentheses. NS=Not sampled. NA=Not analyzed. Amount of carbon collected for each sample is shown in Table D5.

Table D8. VOC EF for each collected sample in lb/lb Carbon.*

Sample #		Benzene	Toluene	Ethylbenzene	Xylene	1,2,4- Trimethylbenzene
M31A1E1	1	8.6E-06	3.4E-04	4.3E-05	2.4E-04	6.0E-05
	2	3.8E-06	2.1E-05	4.8E-06	2.8E-05	8.6E-06
	3	4.4E-06	7.4E-05	1.3E-05	7.8E-05	2.6E-05
	4	2.9E-05	5.0E-04	2.8E-05	1.6E-04	4.1E-05
M26	1	1.2E-05	1.7E-06	ND	9.9E-06	7.2E-06
	2	1.4E-05	2.4E-05	9.8E-06	6.3E-05	2.1E-05
	3	1.6E-05	BBL	ND	4.1E-05	3.2E-05
	4	3.2E-06	2.0E-07	ND	3.2E-06	1.5E-06
	5	ND	9.0E-07	ND	1.1E-05	8.6E-06
SPCF	1	ND	5.8E-06	8.7E-06	7.4E-05	1.2E-04
	2	ND	2.7E-06	ND	8.6E-06	5.0E-06
	3	ND	BBL	ND	ND	7.0E-06
AP Static	1	ND	4.1E-05	ND	1.1E-04	5.6E-05

* ND = Not detected, see Table D9 for detection limits. BBL = Below background level.

Table D9. VOC, CO₂ and CO concentration in each collected summa canister sample.*

Sample #		Benzene	Toluene	Ethyl- benzene	m,p- Xylene	o- Xylene	1,2,4- Trimethyl- benzene	CO ₂	CO
		µg/m ³	µg/m ³	µg/m ³	µg/m ³	µg/m ³	µg/m ³	ppmV	ppmV
M31A1E1	1	1.1 [0.53]	44 [0.57]	5.5 [0.53]	22 [1.1]	8.9 [0.57]	7.7 [0.57]	670 <8.8>	ND <8.8>
	2	1.1 [0.58]	7.1 [0.62]	1.4 [0.58]	5.8 [1.2]	2.4 [0.62]	2.5 [0.62]	1,000 <9.6>	ND <9.6>
	3	1.2 [0.58]	21 [0.63]	3.4 [0.58]	15 [1.2]	6.2 [0.63]	6.9 [0.63]	960 <9.7>	ND <9.7>
	4	3.0 [0.43]	53 [0.47]	2.9 [0.43]	12 [0.90]	4.6 [0.47]	4.2 [0.47]	620 <7.2>	ND <7.2>
M26	1	3.6 [0.48]	1.6 [0.52]	ND [0.48]	1.9 [1.0]	0.97 [0.52]	2.1 [0.52]	1,000 <8.1>	ND <8.1>
	2	1.8 [0.56]	4.3 [0.61]	1.3 [0.56]	5.8 [1.2]	2.5 [0.61]	2.8 [0.61]	680 <9.4>	ND <9.4>
	3	0.69 [0.56]	0.88 [0.60]	ND [0.56]	1.2 [1.2]	0.60 [0.60]	1.4 [0.60]	500 <9.3>	ND <9.3>
	4	3.1 [0.57]	1.3 [0.62]	ND [0.57]	2.1 [2.1]	1.0 [0.62]	1.5 [0.62]	2,400 <9.6>	ND <9.6>
	5	ND [0.68]	1.3 [0.74]	ND [0.68]	1.6 [1.4]	0.82 [0.74]	1.9 [0.74]	860 <11>	ND <11>
SPCF	1	ND [0.56]	1.7 [0.60]	0.90 [0.56]	4.8 [1.2]	2.8 [0.60]	12 [0.60]	620 <9.3>	ND <9.3>
	2	ND [0.62]	2.0 [0.67]	ND [0.62]	2.0 [1.3]	0.91 [0.67]	1.7 [0.67]	1,100 <10>	ND <10>
	3	ND [0.54]	1.1 [0.59]	ND [0.54]	ND [1.1]	ND [0.59]	1.3 [0.59]	790 <9.1>	ND <9.1>
AP Static	1	ND [0.50]	1.5 [0.54]	ND [0.50]	1.1 [1.0]	ND [0.54]	0.55 [0.54]	430 <8.3>	ND <8.3>
Ambient air	1	ND [0.51]	1.1 [0.56]	ND [0.51]	ND [1.1]	ND [0.56]	ND [0.56]	410 <8.6>	ND <8.6>

* ND=Not detected, detection limit within parentheses. Method reporting limit within arrows.